VOL. VII MAY, 1919 No. 5

SOIL SCIENCE

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PUBLISHED MONTHLY BY
WILLIAMS & WILKINS COMPANY
BALTIMORE, MD., U. S. A.

THE CAMBRIDGE UNIVERSITY PRESS
FETTER LANE, LONDON, E. C.

Entered as second-class matter May 12, 1919, at the post office at Baltimore, Maryland, under the act of March 3, 1879.

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Price { $6.00 per year, two volumes, United States, Mexico, Cuba
$6.25 per year, two volumes, Canada
$6.50 per year, two volumes, other countries

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THE CARBONATION OF BURNT LIME IN SOILS[1]

WALTER HOGE MacINTIRE

University of Tennessee Agricultural Experiment Station

Received for publication July 21, 1919

INTRODUCTION

The practice of applying burnt lime to soils has long been followed as one of the fundamental agricultural arts. Particularly is this true in European countries. The scientific principles involved in the practice are, however, of but recent and partial development. During ancient times, the beneficial effects upon soil structure and increased plant growth, following the use of lime, were attributed to the production of a soil condition known as "sweet." From modern investigations, more particularly in the laboratory, it is now known that the benefits derived from the use of lime are due to its effects upon conditions, physical, chemical and biological. The amelioration of unfavorable physical conditions; the eradication of various chemical soil constituents of acid or toxic nature; the supplying, directly or indirectly, of plant-food requirements; and biological betterment have been urged as compelling independent or collective reasons for the application of lime to soils. While the subject of liming, even yet, has had but relatively limited scientific development, the importance of the practical and economical phase of the question has increased to a marked extent. Even in some newly cleared virgin soils, liming is found to be shortly or immediately a profitable treatment; while in the rejuvenation of worn-out and abandoned soils lime is often found to be a prerequisite.

Nevertheless, in some localities even today the need of lime is unrecognized or ignored. In many soils which have long been subjected to cultivation, the continued demand of plants for calcium as a nutrient, together with its loss by leaching, has resulted in a deficiency of lime, which, in some cases, has assumed the proportion of a limiting factor. This is often true in the case of residual limestone soils, formed *in situ*.

With the advent of improved appliances and machinery for tillage, and with the development of more intensive cultivation, the transported calcareous soils of more recent origin are now more rapidily depleted of their lime contents. Better aeration results in greater oxidation of soil organic matter, and it follows that the soil solution will become richer in carbon dioxide. Thus

[1] A thesis submitted to the Faculty of the Graduate School of Cornell University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, September, 1916.

a stronger solvent will be furnished for the dissolving and leaching of mineral calcium carbonate, or for the hydrolyzation and leaching of other forms of lime. Data upon this phase of the subject have been reported by Hall (27) who states: "The Rothamsted soil which at the beginning of the Nineteenth Century must have contained something like a hundred tons of chalk per acre has now less than fifty and many other soils which started with a smaller initial stock are beginning to run dangerously short." Additional data concerning the conservation of lime have been reported also from the Hawaiian Sugar Planters' (12), Florida (4), Maryland (6), Cornell (45, 46), and Pennsylvania (47) stations, and by Gilchrist (25) and others.

The development of modern crushing machinery and the advent of by-product limestone has given a healthy stimulus to the use of lime in the form of ground rock. As a result, the term "liming" has become a synonym for application of either burnt lime or ground limestone. In ancient times the soft chalks of Europe were dug and made available by being brought to a state of fineness through exposure to the disruptive action of weathering. In a more restricted way, wood ashes also were utilized, particularly in vineyard cultivation. However, in localities where neither chalk nor marl was available "burning" of limestone constituted the only practice which afforded an extensive source of agricultural lime. Hence, while, prior to more recent times, the question of liming often involved only consideration, pro and con, of the use of the one available form, the burnt oxide, agriculture of the present day has to consider, both economically and scientifically, the question of burnt lime versus ground limestone. As a natural sequence, there have developed diversity of viewpoint and division of opinion as to the relative merits and diverse or parallel activities of these respective forms of lime. A general comparative study of the lime problem embraces a wide range of investigation, for an unbiased judgment requires abundant data upon which to base a thorough understanding of the complex question. A study of the available literature and experimental findings reveals an amazing lack of fundamental and thoroughly scientific data on the problem of differential liming.

The application of either burnt, air-slaked or water-slaked lime to soils is followed by the phenomena of absorption and carbonation in sequence, or in the reverse order. The existing soil moisture conditions and the manner of applying or incorporating will be the deciding factors in determining the order of the changes, as will be shown in this contribution. If the application is in excess of the immediate absorption coefficient, formation of calcium carbonate from the unabsorbed lime will ensue. The term "immediate lime absorption coefficient" is here used because of the fact that it has been shown by the writer (47, 48) that there occurs a progressive decomposition of calcium carbonate and absorption of calcium by soil, when soil and calcium carbonate continue in contact under moist conditions This slow, continued absorption, subsequent to the initial rapid absorption, may continue over a period of years. The phenomenon has also been demonstrated, by Bou-

youcos and Laudeman (5), in a different manner over shorter periods. Therefore, an ultimate quantitative chemical comparison between the activities of burnt lime and natural lime rock in soils may well be based upon periodically determined occurrences of $CaCO_3$. Such a requirement necessitates a careful study of the factors influencing or controlling the carbonation of burnt lime in soils. This dissertation is intended to embody results obtained in carrying out field-exposure and laboratory experiments on this particular phase of the complex lime problem. It is not intended to incorporate those data which have been secured on the somewhat related questions of supposed base substitution, quantitative biological and physical effects, although to some extent these factors are necessarily considered.

HISTORICAL

In the practice of applying lime, the caustic may be so exposed or handled as to become, in large measure, carbonated prior to its contact with the soil. Or, again, it may be converted to the carbonate while lying on the surface of a dry soil or dust mulch, before its incorporation with the body of the soil. Such a condition of dry surface contact would minimize, if not prevent, absorption until admixture of soil and carbonate were effected. It thus becomes necessary first to consider the conversion of oxide and hydrate to carbonate, under conditions where the factor of absorption by the soil is eliminated.

Though qualitatively a well-known chemical reaction, the conversion of CaO or $Ca(OH)_2$ to $CaCO_3$, following exposure, has received but little attention quantitatively. Expressions of opinion are to be found, and some data are to be cited from authoritative sources, however, but few controlled experiments are available for reference. Gillmore (26) states that complete carbonation of some limes may take place within 20 to 25 days in layers approximately one foot in depth, while under the same conditions other limes may require as long as a year to effect complete carbonation. Vicat (68) claims that at the end of one year's time the carbonation of a layer of "fat" lime in free contact with the atmosphere extends to a depth of 0.10 to 0.12 inch. Eckel (13) states that the hydrated lime within the body of wall plaster never undergoes carbonation, because of the protecting action of the $CaCO_3$ layer. Lloyd (44) states that ordinarily when high-grade burnt lime is exposed in the field and slaked under natural climatic influences, large heaps of lime will become pulverized by spontaneous slaking within 4 to 6 weeks. He cites an analysis of a 99 per cent lime so treated as showing 15 per cent $CaCO_3$ and 83.4 per cent $Ca(OH)_2$. Kellner (39) placed compact circular piles of slaked lime under shelter and found after free exposure for 8 weeks, that only 3 per cent of the lime had become carbonated, no further increase being found subsequent to that period. Frear (21) states that his examination of a sample of burnt lime taken 4 inches from the surface of a large pile 10 years old

showed but 10 per cent carbonation. Burchard and Emley (7) report that analyses of 11 samples of commercial fine hydrated lime in bags gave an average of 8.57 per cent $CaCO_3$. The time intervening between hydration and analysis was not given. These writers also gave figures obtained by them in comparative studies of the rate of carbonation of burnt and hydrated lime. Samples of 60-mesh materials were exposed for 10 days and analyzed 6 times during the interval. The carbonation of the hydrated lime was consistently greater throughout, and at the end of 10 days its percentage of CO_2 was 11.25 as compared to 8.73 for the quicklime. These data are particularly interesting when compared with those of tables 3 and 4, in which the reverse is recorded. Feilitzen (15) made the interesting observation that the steam generated in the water-slaking of lime produces a hydrated lime more finely divided than that obtained from air-slaking. The latter gave 52 to 75 per cent of screenings finer than 2 mm. This might be attributed to the granulation following the greater partial carbonation of the air-slaked lime. This observation is interesting in view of the statement by Eckel (13) that if the full required amount of water be added at once to a pure lime the bulk will be increased $3\frac{1}{2}$ times, while air-slaking effects an increase in volume of but 1.7 times that of the burnt lime. Frear (22) cites data obtained through personal correspondence to the effect that 7 per cent of a 40-pound sack of hydrated lime had carbonated at the end of one year, while 14 per cent had been converted into the carbonate form at the end of 2 years. Wheeler (69), reporting upon the composition of air-slaked lime used by the Rhode Island Station, states that the amounts of CaO have varied from 68 to 75 per cent. The writer has made periodic observations of piles of a bushel or less of slaked lime, where it was evident that no appreciable carbonation of the hydrate occurred beyond a thin surface layer, unless sufficient moisture were present to cause extensive cracking and checking of the mass during drying.

Subsequent to the drafting of the manuscript of this thesis, and after completion of the analytical work reported, a most interesting article, by Woodhead (73), has appeared in print. Woodhead studied the reversion of freshly burnt powdered and lump CaO, under different conditions of exposure. Two hundred pounds of freshly burnt lump lime were powdered and subdivided into 100-pound lots. One 100-pound portion was spread on a dry floor and turned and respread daily for 64 days. Residual CaO determinations were made periodically by the 10 per cent sugar solution method of Hendrick (32). The initial CaO content decreased to 63.3 per cent after 10 days; to 57.12 per cent after 20 days; to 52.36 per cent after 30 days; to 47.18 per cent after 40 days; to 45.31 per cent after 50 days and to 39.48 per cent after 64 days. This represented a total CaO decrease of 29.62 per cent, equivalent to 43 per cent of the original CaO. The second 100-pound lot of powdered CaO was immediately dumped outdoors, where it was subjected to weather for a period of 4 months, after which time it was found

to be covered with a crust devoid of CaO. The interior of the pile showed a residual CaO content of 66.92 per cent. The average CaO content determined by the analysis of the mixed crust and interior was found to be 60.83 per cent. This represents a CaO decrease of less than 12 per cent.

Another sample of 200 pounds was exposed in the lump condition. One lot of 100 pounds was bagged and exposed under shelter. After 4 months this sample was mixed and found to contain 50.26 per cent residual CaO as compared to an original content of 81.2 per cent. The second portion of 100 pounds of lump CaO was exposed to the elements for a period of 4 months, at the end of which time the crust gave a residual CaO occurrence of 1.82 per cent, while the interior contained 54.88 per cent CaO. The mixed sample of crust and interior gave a percentage of 38.78 CaO as compared to the original content of 81.2 per cent.

Woodhead's findings, as summarized by him, are:

(1) Powdered lime—dry shed exposure and frequent turnings—deteriorated 43 per cent in 64 days.

(2) Powdered lime—heaped outside, complete exposure—deteriorated 12 per cent in 4 months.

(3) Bagged lump lime—sheltered outdoors—deteriorated 38 per cent in 4 months.

(4) Heaped lump lime—exposed to elements for 4 months—deteriorated 52 per cent.

It would appear that the crust formed over the surface of the powdered CaO exposure served as a watershed and as a layer relatively impervious to an infusion of CO_2. The same protective action of $CaCO_3$ will be shown later to hold for smaller quantities in laboratory studies.

In the discussion following the presentation of Woodhead's paper, Dr. Voelcher, of the Woburn Station, offered data on the subject. These data were secured by comparisons made in 1910 and 1916 upon surplus quantities of lime used in lime experiments at the Woburn Station. The residues were kept in covered wooden tubs.

PER CENT OF TOTAL LIME IN	BUXTON LIME	CHALK LIME	MAGNESIAN LIME	LIOS LIME	OOLITE LIME
1910	92	95	60	70	75
1916	74	80	54	55	65

From these analyses, Dr. Voelcher concluded that less deterioration in burnt lime would be encountered than would be indicated by Woodhead's results.

Considering the carbonation of burnt lime, with reference more particularly to soils, we find some decided opinions as to the phenomenon, but a dearth of data. Heinrich (31) contends that lime reverts to the carbonate very quickly after its application to soils. Storer (63) states, "It is not to be supposed that in the field, reactions due to causticity of the lime can go

on for any long period." According to Frear (19), "There is considerable doubt upon this question. . . . . It is generally conceded that the lime must be carbonated almost immediately after it is spread and harrowed in," and "it is almost necessary to assume that lime cannot long remain caustic after it has been spread and worked into the soil in a finely divided state." Storer (63), citing without reference the work of Heiden, states, "But recent investigations by Heiden go to show that a part of the lime may remain in the soil for years in the soluble form, at least on lands that have been heavily limed. Heiden argues that the lime soluble in water was chiefly in the form of hydrate of lime, because the soil had an alkaline reaction and because he found comparatively little carbonic acid in the solution." Apparently the fact was overlooked that CO_2-treated precipitated $CaCO_3$ and the mineral carbonates of calcium will hydrolyze and give alkalinity indications in both cold and hot distilled water and in absence of free CO_2, even when phenophthalein is used as an indicator. This has been demonstrated by the writer (49).

Fippin (16) writes, "While lime in large lumps air-slacks relatively slowly, when in the fine powder in which it should be incorporated in the soil, the change is rapid. We know of no determinations of the rate of this change in the soil and we do not see how it can be accurately determined in normal soil; but there is much reason to believe that the reversion would be complete in a few weeks at most." The writer has been able to find only one attempt to determine quantitatively by chemical means the rapidity of carbonation of burnt lime in soils. This work was reported by Dr. Wm. Frear in 1899 (20). Nine soils, all being acid in reactions to litmus, were mixed with freshly burnt lime at the rate of 10 gm. per 2000 gm. of air-dried soil. They were then moistened with water and permitted to stand for 10 months, further additions of water being made during the first 3 months. At the end of the 10-month period, the soils were again air-dried and analyzed for CO_2. The analyses when averaged showed that, of the CaO added, 28 per cent had reverted to $CaCO_3$. While it was recognized that the CO_2 analyses did not establish the absence of residual CaO from that applied, it was believed by Frear that, "Considering the relatively large quantity applied, it is difficult to conceive that a very large fraction has not remained in caustic condition." Dr. Frear further states, "The evidence favors the belief that the conversion of caustic lime to carbonates in the soil may be much less rapid than has been heretofore assumed." Quite unfortunately, in this experiment no precipitated $CaCO_3$ checks were included, as parallel treatments. Hence, it is difficult to say how much of the uncarbonated CaO was used to satisfy the tendency of the soil to absorb lime. On the other hand, restricted diffusion of atmosphere to the soil, and probable decreased biological activities as a result of partial sterilization from the excess of CaO, may have depressed the generation of CO_2, thus permitting some of the applied lime to remain as hydrated lime. More recently biological activities have been used at the Rothamsted Station (37) as a means

of indicating the period required for complete reversion of lime to carbonate. It is stated in this work that chemical studies will be reported later (38).

Hoagland and Christie (33), in a recent article, state " . . . . but the assumption is generally made that carbonation quickly takes place, so that the ultimate effect is the same as though the carbonate had been used in the first place." The same authors, in hydroxyl-ion concentration studies, noted a rapid decrease from the immediate and maximum concentration within a few days after additions of CaO to several soils, though the OH-ion concentration continued for a long time in excess of that of the original alkaline soils, and also that of the alkaline soils, which received $CaCO_3$ equivalent to the applications of CaO, which applications were at the rate of 0.07 per cent and 0.28 per cent CaO. The authors state that, "After the first few days the alkalinity decreases in all soils, either because of continued chemical action or of slow reaction with CO_2."

In another experiment the same authors treated an acid fine sandy loam with 0.5 per cent CaO, using an equivalent quantity of $CaCO_3$ as a check. After one year's exposure, "The soil treated with $CaCO_3$ gave an exponent of 8.05, while that treated with CaO gave 11.34. The latter represents an intense alkalinity, and it is clear that complete carbonation did not take place even after a long period of time." The admixtures of lime were throughout the entire body of the soil, and it is assumed that the sampling was representative of the whole mass. From the data offered in tables 32 to 35, it is evident that carbonation takes place much more rapidly in the surface than in the lower stratum of a soil treated with CaO. It is quite possible that a like condition existed in the soils studied by the authors above named. However, the data which will be offered in the cylinder and lysimeter studies strongly indicate that with applications in excess of the lime absorption coefficient more CaO is absorbed by the soil from CaO and $Ca(OH)_2$ treatments than from equivalent amounts of $CaCO_3$. This means that heavy CaO and $Ca(OH)_2$ treatments produce a greater mass of freshly formed silicates. These silicates readily undergo hydrolysis, and to the writer it would seem as reasonable to assume such to be the cause of an excess of OH-ion as to attribute the alkalinity to residual $Ca(OH)_2$ from applied CaO. As a matter of fact, Plummer (54) found, when examining certain soils which were sent to him by the writer, that the OH-ion concentration was very marked as the result of hydrolysis of silicates which had been formed from applied carbonate, though the latter had entirely disappeared many months prior to the ion-concentration studies.

CHEMISTRY OF THE CARBONATION OF BURNT LIME

Historical

There appears to be some confusion in the general usage of the term "air-slaked lime." This fact was taken into consideration by Emley (7). He states that the Bureau of Standards has adopted the term "water-slaked

lime" to designate the product resulting from the hydration of CaO, while the term "air-slaked lime" is used to designate the carbonate end product. The reversion of burnt lime to the carbonate is considered as proceeding through the stages

$$CaO + HOH \rightleftharpoons Ca(OH)_2 \text{ and } Ca(OH)_2 + CO_2 \rightleftharpoons CaCO_3 + H_2O,$$

when exposure is permitted under normal conditions. While it has generally been conceded that the hydration of lime precedes its carbonation, and that this order is due to the fact that the atmosphere affords more of moisture than of CO_2, very few data on the question of relative affinities of H_2O and CO_2 for CaO were available. This phase of the problem has considerable bearing upon the control of experimental conditions in some of the soil studies. In the planning of the experimental work, certain contingencies incident to the sampling, preparing and bottling of the treated soils at successive periods were anticipated. This necessitated the securing of data relative to errors which might be expected to result from carbonation of the hydrate in samples during the process of handling and preparation for analysis. In some instances, of necessity, many hours elapsed between the bottling of the first and last samplings of the large number which were taken at the same period. It was thus essential to submit all of the samples collected at a particular period to treatment which would effectuate conditions that would quickly terminate carbonation. The most feasible procedure seemed to be that of drying the soils in an electric oven, at a temperature which would quickly free the soil containing lime, still uncarbonated, from its dissolved and free CO_2 and at the same time stop the generation of CO_2. It was, therefore, necessary to determine whether, at relatively low temperatures, lime devoid of moisture would cease to be susceptible of conversion to the carbonate. The literature and a few references were supplemented empirically. Mendeleeff (52) states that anhydrous lime will not combine with dry carbonic anhydride, citing Scheele as authority. Schuliachenko is also quoted as stating that the combination does not take place, even at 360°. Mendeleeff further states that, "if the lime is slaked or dissolved, the absorption of carbonic anhydride proceeds rapidly and completely." If by this is meant that dry slaked lime will combine with dry CO_2, that the solid phase of $Ca(OH)_2$ will combine with dry CO_2, the foregoing statement is not susceptible of proof. Veley (66), in 1893, studied "the inertness of quicklime" and pointed out the unreliability of the few observations which had been recorded at that time. Veley demonstrated the inactivity of CaO toward CO_2 and toward SO_2 and the oxides of nitrogen. In Veley's experiments the gases were passed over the lime during the period of ignition. However, working with open platinum crucibles, and using coal-gas for ignition, the writer found an extensive reaction between SO_2 and lime heated to a white heat. This was followed by oxidation to sulphate. Three charges of 0.6 gm. of sulfur-free CaO were ignited continuously for 2 weeks over Bunsen burners. At the end

of that time, the charges had materially increased in weight. Upon test, it was found that the CaO was heavily impregnated with $CaSO_4$. The ignition was repeated on another sample, with the following results. A charge of 0.6 gm. of marble-derived $Ca(OH)_2$, sulfur-free, was ignited continuously for a day and two nights. It was then dissolved and sulfates determined. A weight of 0.0881 gm. of $BaSO_4$, equivalent to 0.0513 gm. $CaSO_4$ was obtained.

In a later article Veley (67) also considers the quiescence of dry chlorine toward CaO. Veley offers in the first-cited article the only comparison originally available to the writer, in which the oxide and hydrate are considered in parallel. Though he does not establish the absence of reaction between dry $Ca(OH)_2$ and dry CO_2, he does show that the amount of water added to CaO is a factor in determining the extent of the reaction within a given time He also shows that the addition of uncombined water to $Ca(OH)_2$ is followed by a marked increase in the tendency of the hydrate to absorb CO_2. He further concludes: "It would, therefore, appear that it is necessary for the reaction that both the hydrate and the carbon dioxide should be dissolved in the water, and the change is incomplete when the gas has only the chance of being dissolved in the water which it succeeds in driving out from the hydrate."

Since most of the experimental work offered in the following pages was completed, the writer has secured a copy of the report of the Columbus (Ohio) Division of Water for the year 1915, in which is incorporated work done by Hoover (34) in a study of the storage of burnt lime. His observations on the changes in volume effected by contact of CaO and $Ca(OH)_2$ with dry and moist air, both with and without CO_2, led to the statement that "the process of hydration takes place first, and . . . . carbonation does not begin to any great extent until after the lime has been completely hydrated." His work further indicated a minimum reaction between $Ca(OH)_2$ and CO_2 in the absence of uncombined H_2O. He also obtained interesting data to the effect that the degree of humidity, as influenced by seasonal changes, is the controlling factor in the speed of the formation of $CaCO_3$, when CaO is exposed in bulk under practical conditions.

Experimental

As to the behavior of dry CaO *toward dry* CO_2. This phase of the problem was considered and tested experimentally in quadruplicate, as follows:

Freshly burnt lime from 0.5-gm. charges of $Ca(OH)_2$, 99.76 per cent pure, were placed in glass-stoppered U-tubes. These were then maintained at a temperature of 105°C. for an overnight period, during which time a current of dried CO_2-free air was drawn through the containers, in order to remove all moisture vapor. The tubes were then cooled and weighed. The weighed tubes were then connected with a CO_2 generator and currents of moisture-free CO_2 were passed over the dry CaO at room temperature for periods of 5 hours.

The CO_2 atmosphere was then displaced by dry CO_2-free air and the tubes again weighed. Drying of the air and CO_2 currents was effected by slow passage through a Greiner-Friedrich absorption tower containing concentrated H_2SO_4. The data in table 1 were obtained.

TABLE 1

Change in weight of tubes containing dry CaO *after passage of dry* CO_2

Determination A	Change of + 0.0028 gm.
Determination B	Change of − 0.0004 gm.
Determination C	Change of − 0.0009 gm.
Determination D	Change of + 0.0012 gm.

Successive daily weighings of the empty tubes and counterpoises showed the above differences to be within limit of error of weighing. A second passage of dry CO_2 for a period of $3\frac{1}{2}$ hours in each case confirmed the above results. During the period of exposure of dry CaO to dry CO_2, 19.4 gm. of the gas passed over each of the charges of oxide. The foregoing data demonstrate that dry CaO and dry CO_2 will not combine chemically at room temperature. This would indicate one of two possibilities, as an essential condition for carbonation—either moisture must be present as a catalytic agency to initiate reaction, or else it is necessary that the reaction proceed through the stage of chemical combination with H_2O, thus: $CaO + HOH \rightleftharpoons Ca(OH)_2$, followed by the combination with CO_2, thus: $Ca(OH)_2 + CO_2 \rightleftharpoons CaCO_3 + H_2O$.

The behavior of dry $Ca(OH)_2$ *toward dry* CO_2. The activity of dry powdered $Ca(OH)_2$ toward dry CO_2 was then studied. Charges of 0.5 gm. of the $Ca(OH)_2$, from which was obtained the CaO used in the preceding work, were dried overnight in an electric oven at 105°C., with aspiration of dry CO_2-free air. Then, after attaining room temperature, the tubes were weighed and a current of CO_2, dried as previously described, was passed over each of the four charges of $Ca(OH)_2$, for a period of 5 hours. Eleven and four-tenths grams of CO_2 were passed through each tube. The data in table 2 were thus secured.

TABLE 2

Change in weight of tubes, containing dry $Ca(OH)_2$ *after 5 hours passage of dry* CO_2

Determination A	Change of + 0.0019 gm.
Determination B	Change of + 0.0022 gm.
Determination C	Change of + 0.0022 gm.
Determination D	Change of + 0.0018 gm.

These data demonstrate either an exceedingly minute chemical reaction between the dry hydrate and the dry gas, or probably no reaction at all. As before stated, blank determinations were run with the counterpoises and these showed that the above amounts are well within experimental error, under conditions encountered from day to day. The small plus indications are due, possibly, to a constant plus error from comparable manipulation.

In this connection it might be contended that the preliminary heating to eliminate moisture would effect a possible molecular change, which might serve to retard carbonation that would have readily ensued with the original hydrate. This was shown not to be the case. In so doing duplicate charges of 0.3 gm. of hydrated lime were placed in 300-cc. Erlenmeyer flasks and exposed to the *outdoor atmosphere* simultaneously with duplicate charges which were first heated overnight in an electric oven at 120°C. Each charge was intimately mixed with dry sawdust, prior to exposure, in order to afford uniform and extensive surface for carbonation. At the end of 6 days, the CO_2 determinations on the four samples gave an average of 16.16 per cent of theoretical carbonation, for both the heated and the unheated charges.

The tendency of reheated $Ca(OH)_2$ *to revert to* $CaCO_3$. However, working with small charges, the effect of long heating at high temperature produced an entirely different result, and one different from what would seem at first thought reasonable to anticipate. Instead of retarding the speed of the carbonate reaction, the additional heating of $Ca(OH)_2$ and its reversion to CaO accelerated the carbonation reaction. This was demonstrated in the following manner: Charges of 0.3 gm. of dry high-grade $Ca(OH)_2$ were ignited for 16 hours over Bunsen burners. At the end of that period, the crucibles were cooled and the charges pestled and thoroughly mixed with dry sawdust. The untreated $Ca(OH)_2$ was weighed, ground and mixed in the same manner, at the same time. Though carefully pestled, the CaO charges could not be considered as strictly comparable in fineness with the pulverulent hydrate obtained by steam slaking. Each of the several charges was then placed in a 300-cc. Erlenmeyer flask and the flasks were exposed side by side for 7 days in a sheltered exterior. At the end of that time, the contents of each flask were subjected to analysis. The ignited charges had extracted almost twice as much CO_2 from the atmosphere as had the unignited ones. This was first done in duplicate, with 0.3 gm., and later checked twice by repetition in triplicate, with both 0.3 gm. and 0.5 gm. charges. In the second and third exposures, constant amounts of acid-washed quartz sand were substituted for the sawdust. The analyses of each series are given in table 3.

The chemically equivalent charges of CaO and $Ca(OH)_2$ functioned differently toward the moisture vapor accessible to the exposures within the flasks. The CaO exerted a chemical attraction resulting in the transition of the CaO to a new chemical compound, $Ca(OH)_2$, while the $Ca(OH)_2$ could only extract moisture through the physical function of surface. It would seem, therefore, that the equal quantities of moisture vapor available to small charges of both CaO and $Ca(OH)_2$ during normal humidity would have effected a greater conversion of hydrate rom solid to solution phase in the compound which had already taken up the amount of water essential for hydration. It appears, however, that the nearly simultaneous hydration and carbonation, possible with the CaO, was responsible for a more rapid formation of $CaCO_3$. Parallel observations with CaO, practically free of silica, as

compared to the same substance after extensive reheating, demonstrated that the additional blasting exerted no depressing effect upon the tendency of the lime to combine with moisture vapor. The experiment, therefore, resolves itself into a comparison between the speed of the formation of $CaCO_3$ from exposures of CaO, and that resulting from simultaneous exposures of chemically equivalent amounts of $Ca(OH)_2$, under the atmospheric conditions encountered. While the differences found might be considered as resulting from a possible molecular readjustment, consequent upon re-heating the hydrated oxide, they are more probably due to the nascency of the reheated oxide and the opportunity for almost simultaneous hydration and carbonation.

TABLE 3

Extent of carbonation resulting from simultaneous outdoor exposures of $Ca(OH)_2$ *and* CaO *obtained by ignition of* $Ca(OH)_2$

	DETERMINATION	PER CENT $CaCO_3$ OF THEORY	
		Unblasted	Blasted
1	A	11.83	31.83
	B	10.72	27.35
	C	10.08	26.71
2	D	17.75	29.91
	E	14.71	30.87
3	F	28.96	36.57
	G	30.12	37.87
	H	30.12	37.49
	Average	19.28	32.33

1. 0.3 gm. exposure with sand, October 12–19.
2. 0.3 gm. exposure with sawdust, October 5–12.
3. 0.5 gm. exposure with sand, October 30 to November 6.

The foregoing results do not bear out the statement of Emley (7), to the effect that $Ca(OH)_2$ will revert to the carbonate more rapidly than will CaO. It seemed quite possible that the question of season, particularly as it affects humidity, might account for the divergence. The further factor of the influence of the size of the charge in its effect upon the moisture and CO_2 vapor pressures in the containers was taken into account. The charges exposed, as shown in table 4, varied from a minimum of 0.3 gm. to a maximum of 2.4 gm. of hydrate. It should probably be emphasized that the hydrate was well slaked and exceedingly pulverulent. Baker's analyzed oxide from burnt marble was used as the source of the hydrate. The oxide was carefully slaked by action of steam generated by the hydration. The mass was then brought to the consistency of a thin paste by further additions of distilled water. It was then dried in a closed flask by heating and aspirating off all

free moisture in a CO_2-free atmosphere. One-half of the number of weighed charges of hydrate were blasted for 30 minutes and the remaining ones were exposed unaltered. The blasted charges were quickly pulverized after cooling. Each charge of hydrated lime and each charge of the blasted oxide was mixed with an asbestos-soapstone mixture and exposed simultaneously. In this way chemical equivalence was maintained and as uniform surface as possible was attained. However, even with careful pulverization the freshly burnt oxide presented far less surface than was offered by the hydrate. In this connection it is of interest to note that the hydrate and oxide charges exposed by Emley were of but 60-mesh fineness.

TABLE 4

Showing extent of carbonation from simultaneous outdoor exposures of $Ca(OH)_2$ *and* CaO *obtained by ignition of* $Ca(OH)_2$

EXPOSURE CONDITIONS			MIXTURE	CHARGE OF ORIGINAL $Ca(OH)_2$	CORRECTED PER CENT CARBONATION	
Period	Season	Atmosphere			Original $Ca(OH)_2$	CaO obtained by ignition of original $Ca(OH)_2$
hours				*gm.*	*Per cent*	*Per cent*
48	June	Humid	Lime and silicate	0.30	31.40	54.37
48	June	Humid	Lime and silicate	0.30	40.54	48.85
48	June	Humid	Lime and silicate	0.30	40.54	51.96
48	June	Humid	Lime and silicate	0.30	39.57	49.54
48	June	Humid	Lime and silicate	0.60	31.85	41.34
48	June	Humid	Lime and silicate	0.60	32.11	40.80
48	June	Humid	Lime and silicate	0.60	32.65	39.41
48	June	Humid	Lime and silicate	1.20	16.59	22.96
48	June	Humid	Lime and silicate	1.20	13.99	21.38
48	June	Humid	Lime and silicate	1.20	12.51	18.73
48	June	Humid	Lime and silicate	2.40	7.82	16.59
48	June	Humid	Lime and silicate	2.40	8.61	20.81
48	June	Humid	Lime and silicate	2.40	9.17	18.01
48	June	Humid	Lime and silicate	2.40	9.97	20.37
Average				1.157	24.53	33.22

The second series of exposures of table 4, made during the month of June and under humid conditions, follow the same trend as those of table 3. However, the influence of humidity is very apparent in its effect upon the actual amount of carbonation effected. With 7 days of exposure during October, an average of the carbonation attained by five 0.3-gm. and three 0.5-gm. charges of unblasted hydrate gave 19.28 per cent as against 32.33 per cent for the blasted hydrate as was shown in table 3. On the other hand, with 48 hours exposure during June, the average per cent carbonations of 41.44 and 54.38, respectively, for the unblasted and blasted hydrates were attained. The influence of moisture vapor in the conversion of the hydrate from the

solid to solution phase is very marked. It is interesting to observe that with the increase in charges the carbonation results become less uniform. This decrease in concordance with increase in charge is particularly noticeable to the analyst.

In each of the 14 simultaneous exposures of table 4 the oxide, obtained by re-heating the $Ca(OH)_2$, gave a more extensive carbonate formation. The larger actual amount of CO_2 absorbed by the 2.4-gm. charges, as compared with the 0.3-gm. charges, indicates that the smaller charges did not effect complete fixation of the amounts of CO_2 which were diffused into the flasks and over the surfaces of the charges.

In a further comparison, the factor of re-heating the oxide was eliminated. In this set Baker's analyzed CaO, derived from marble was compared with $Ca(OH)_2$ derived from the same, burnt lime. The complete hydration of the oxide was accomplished in the same way as described in referring to the exposures of table 4. The results of the third exposure are given in table 5. In this experiment it was intended to expose both chemical equivalences and equal weights of the oxide and hydrate. However, in the exposures of June 30 and July 1, the CaO charges were but 86.33 per cent of the equivalence represented by the $Ca(OH)_2$ charges. This inadvertence was caused by the weighing of hydrate charges from another sample of hydrate. The values of the two substances were ascertained by solution and titration of excess of acid. The amount of CO_2 held by each substance was also determined and correction made therefor. In the charges of June 3 and 5 exact chemical equivalence was secured while the exposures of June 10 were made with equal weights.

In the two exposures of the 0.3-gm. and 0.6-gm. charges of hydrate and the 0.2091-gm. and 0.4182-gm. charges empirically determined to be of but 86.33 per cent equivalence, the same relationship was found, as was shown in tables 3 and 4. The first exposure was made under conditions of excessive humidity while the second was made under normal conditions. The average of 23.44 per cent for the first two CaO exposures as compared to 14.52 per cent for the corresponding exposures of $Ca(OH)_2$ represent a very considerable analytical difference. It should also be remembered that the CaO exposures in these two instances represented but 86.33 per cent of the chemical equivalence of the hydrate. It should also be stressed that the pulverulent hydrate, made by steam, engendered by the action of hydration, was considerably finer than the oxide, though the latter was carefully pestled.

As in the case of the reburnt and original hydrate comparisons, it is particularly interesting to note the extent of carbonation of the eight charges of hydrate and the eight charges of chemically equivalent oxide under the 7-day periods of exposure with normal humidity during October, as contrasted with extent of carbonation shown by similar charges during the more humid weather of June and July. The averages of 19.28 per cent and 32.33 per cent carbonation for $Ca(OH)_2$ and CaO, respectively, from a 7-day period

of exposure during October, are comparable with corresponding averages of 14.52 per cent and 23.44 per cent from eight charges of each $Ca(OH)_2$ and CaO during June and July exposures averaging but 32 hours.

In the case of the larger exposures of table 5 we have, however, the reverse of the findings with the lesser charges. The exposures of 1.9372 gm. of CaO

TABLE 5

Additional simultaneous exposures of CaO *and* $Ca(OH)_2$ *in amounts chemically equivalent and also in equal weights. Lime charges mixed with* CO_2*-free siliceous materials*

EXPOSURE		AMOUNT OF CHARGE		HUMIDITY	CORRECTED FOR PER CENT CARBONATION	
Date	Period	CaO	$Ca(OH)_2$		CaO	$Ca(OH)_2$
	hours	*gm.*	*gm.*		*per cent*	*per cent*
June 30	20	0.2091*	0.3000	Excessive	18.93	13.70
June 30	20	0.2091	0.3000	Excessive	18.19	13.54
June 30	20	0.2091	0.3000	Excessive	28.98	15.78
June 30	20	0.2091	0.3000	Excessive	18.75	14.66
July 1	44	0.4182*	0.6000	Normal	26.13	14.22
July 1	44	0.4182	0.6000	Normal	27.90	15.82
July 1	44	0.4182	0.6000	Normal	22.97	12.93
July 1	44	0.4182	0.6000	Normal	25.66	15.49
July 3	24	1.9372	2.4000	Normal	1.43	2.14
July 3	24	1.9372	2.4000	Normal	1.91	3.00
July 3	24	1.9372	2.4000	Normal	1.39	3.00
July 3	24	1.9372	2.4000	Normal	1.28	2.08
June 5	20	2.0505	3.0000	Normal	2.80	4.18
June 5	20	2.0505	3.0000	Normal	2.80	4.76
June 5	20	2.0505	3.0000	Normal	2.65	5.17
June 5	20	2.0505	3.0000	Normal	2.63	5.62
June 10	48	3.0000	3.0000	Normal	6.15	8.88
June 10	48	3.0000	3.0000	Normal	5.73	7.53
June 10	48	3.0000	3.0000	Normal	7.16	9.38
June 10	48	3.0000	3.0000	Normal	4.42	7.57
Average of 0.3-gm. and 0.6-gm. charges, CaO giving greater carbonation					23.44	14.52
Average of 2.4-gm. and 3.0-gm. charges, $Ca(OH)_2$ giving greater carbonation					3.36	5.28

* 0.2091-gm. and 0.4182-gm. charges of CaO represented but 86.33 per cent chemical equivalence of 0.3-gm. and 0.6-gm. $Ca(OH)_2$ charges, respectively, of $Ca(OH)_2$.

and 2.40 gm. of $Ca(OH)_2$, amounts emperically determined as being chemically equivalent, were made by one analyst, while the chemically equivalent charges of June 5 and the equal-weight charges of June 10 were made by a second analyst. The average per cent carbonation effected by the twelve heavy charges of CaO amounted to 3.36, while the corresponding hydrate charges effected carbonation to the extent of 5.28 per cent. The explanation

for this reversal would seem to be that the oxide charge, in its initial period of exposure at least, would be sufficiently large to take into chemical combination, as water of hydration, most of the diffused moisture vapor, thus leaving but little to effect change of the newly formed hydrate from solid to solution phase. This would not, however, prevent localized occurrences of the dissolved hydrate, as is evidenced by the fact that some, though restricted, carbonation took place.

The catalytic action of film moisture in initiating reaction between $Ca(OH)_2$ *and* CO_2. The failure of the dry hydrate of lime to undergo carbonation when exposed to currents of dry CO_2 suggested the possibility of a need of moisture to effect catalysis. As showing the action of moisture in such slight amounts as represented by the moisture film resistant to aspiration of dry air, the following figures are of interest. Equal amounts of CaO, as hydrated oxide, were placed in each of eight glass-stoppered U-tubes. Four of these tubes were subjected to aspiration overnight with dry CO_2-free air.

TABLE 6

Showing carbonation of $Ca(OH)_2$ *as initiated by the film moisture of the weighing tubes*

	OVERNIGHT ASPIRATION AT 105°C, FOLLOWED BY 3½ HOURS' EXPOSURE TO A CURRENT OF DRY CO_2	OVERNIGHT ASPIRATION AT 25°C, FOLLOWED BY 3½ HOURS' EXPOSURE TO A CURRENT OF DRY CO_2
	Increase	Increase
	gm.	*gm.*
Determination A	0.0019	0.0238
Determination B	0.0022	0.0238
Determination C	0.0022	0.0238
Determination D	0.0018	0.0240

Four other tubes were treated in the same manner except that the tubes were maintained at 105°C. during the overnight aspiration. A current of dry CO_2 was then passed slowly through each of the tubes at room temperature during a period of 3½ hours.

The data of table 6 are corrected for the respective determined amounts of water liberated and aspirated after partial carbonation of the hydroxide. These data show that the film moisture, residual from the overnight aspiration with dry air at room temperature, is sufficeint to produce appreciable dissociation of the hydrate followed by determinable carbonation. The passage of dry CO_2 through the apparatus was very slow and additional water was thus made available to effect further dissociation, as the carbonation proceeded. The carbonate conversion effected in this way represents but 13.44 per cent of theory. Thus the rapidity of the actual conversion of the calcium hydrate from solid to solution phase governs the speed of the carbonate reaction. This may prove to be an important factor in determining the speed of the carbonation of lime lying on the surface soil, in that

the prevailing humidity would affect the amount of moisture available for the dissolving of the hydrate.

The hydration of freshly burned CaO *in a moist atmosphere.* As bearing on certain comparisons between the carbonation of CaO and that of $Ca(OH)_2$ in soils, which will later be considered, it was desirable to ascertain to what extent of theory and with what speed the conversion of oxide to hydrate would transpire in the presence of excessive amounts of moisture vapor. This was done under the following conditions.

The charges of table 1 were subjected for 18 hours to a current of CO_2-free air which was saturated with moisture by circulation through distilled water in a Greiner-Friedrich absorption tower at 25°C. The longer period of contact was given in order to insure an amount of water approaching more nearly the quantity of CO_2 passed over the oxide. The water passed over each oxide charge amounted to 1.9378 gm., of which an average of but 0.1095 gm. was absorbed. After passage of moist air, the tubes were again restored to original dry conditions and weighed with the results set forth in table 7.

TABLE 7

Change of weight of CaO *containing tubes after passage of moist* CO_2*-free air*

Determination A	Increase of 0.1056 gm.
Determination B	Increase of 0.1080 gm.
Determination C	Increase of 0.1094 gm.
Determination D	Increase of 0.1148 gm.

Allowing for CO_2 impurities, the hydration calculates to approximately theoretical requirement. The data above demonstrate that the conversion to the hydrate is very rapid when sufficient atmospheric moisture vapor is available.

Relative activities of currents of dry and moist CO_2 *upon charges of dry* $Ca(OH)_2$. The influence of an atmosphere saturated with reference to CO_2 and H_2O, in affording opportunity for chemical reaction between the strongly dissociated, moist, $Ca(OH)_2$ and the hypothethical acid, H_2CO_3 was next studied. The dry $Ca(OH)_2$ was placed in glass U-tubes and subjected to a current of moist CO_2 for a period of $3\frac{1}{2}$ hours. The current of CO_2 was saturated with moisture by slow circulation through Greiner-Friedrich absorption towers. The moist atmosphere, together with the chemically liberated H_2O was then displaced from the tubes by means of overnight aspiration with dry air. The tubes were then weighed and correction applied for the theoretical moisture liberation.

The increase in CO_2, shown in table 8, represents on the basis of theory a percentage carbonation of 35.58. This does not mean, however, the completion of the total carbonation that could be effected in a given time under the chemical conditions imposed; for, as will later be shown, the apparent attainment of chemical equilibrium is due to the protective coating of carbonate which surrounds the enclosed nuclei of hydrate.

TABLE 8

The action of dry and moist currents of CO_2 *when passed over* $Ca(OH)_2$ *for* $3\frac{1}{2}$ *hours*

	GAIN IN CO_2	
	Dry gas	Moist gas
	gm.	*gm.*
Determination A	0.0019	0.0829
Determination B	0.0022	0.0834
Determination C	0.0022	0.0848
Determination D	0.0018	0.0823

METHODS OF ANALYSIS USED IN SOIL STUDIES

In the work embodied in this thesis, the speed of the carbonate reaction was determined by periodic analyses to establish the extent of accumulations of calcium carbonate resulting from applications of CaO and $Ca(OH)_2$, under the several conditions and with varying amounts. This necessitated the making of a large number of CO_2 determinations. The method followed was that of the liberation of carbonate CO_2 by treatment with HCl, 1 plus 9, and the determination of the liberated CO_2 according to the procedure advanced by MacIntire and Willis (50 a, b).

In the analyses of the 2 and 8-ton treatments of the field cylinders, the absorption of the liberated CO_2 was accomplished gravimetrically through the use of soda-lime and sulfuric acid tubes. In the case of the heavier treatments of the tanks sodium hydrate solution was used to effect absorption of the liberated CO_2. At first the amount of CO_2 absorbed by the hydrate solution was determined by the double titration procedure of Brown and Escombe as perfected by Amos (1). This method of absorption extracts all CO_2 and gives very good results in the case of small amounts of carbonates formed from the CaO of the lighter treatments. However, with heavy applications, it was found that the excessive CO_3 ionization of the carbonate solution resulted in an indefinite endpoint and a tendency toward low results. This source of error was noted also by Lunge (41). Later the same writer (42) advocated the use of NaCl to obviate the difficulty. This tendency necessitated either the use of a factor or the addition of salt to the absorbent solution; or else the temperature precautions described by Lincoln and Walton (43). The method of absorption advocated by Tacke (64) in his lime-requirement method was then substituted. This procedure involves the absorption of the CO_2 gas in NaOH, or KOH, followed by precipitation of the normal carbonate by addition of $BaCl_2$ and subsequent determination of residual hydrate. The absorption towers were washed out with CO_2-free water and the washings plus $BaCl_2$ solution made to a volume of 500 cc. After the settling of the barium carbonate, a 200-cc. aliquot of the clear supernatant solution was drawn off and titrated, phenolphthalein being used as an indicator. One-half normal NaOH absorbent solutions were used in the analyses reported in this thesis.

Persistence of hydrated lime in soils

There appears to be no unanimity of opinion as to the persistence of lime in the hydrated form, subsequent to its incorporation with the soil. Since there exists such a great difference between the solubility of $Ca(OH)_2$, and that of $CaCO_3$ derived therefrom, it is to be expected that the function of a definite amount of lime in a soil will be governed by the form in which it remains in the soil. Granting that a large amount of lime has accumulated in a soil over a period of years, from a series of applications of reasonable amounts of CaO or $Ca(OH)_2$, it is difficult to assume that the free water of the soil would contain the hydroxide because of the continued generation of CO_2, which is to be found in both soil water and soil atmosphere. There is also a great difference in the ionic dissociation of equal amounts of dissolved lime occurring in the relatively dilute soil solutions of the two forms of lime. These inherent differences are of importance from both chemical and biological viewpoints and the question of the continued presence of calcium hydrate in soil, treated repeatedly with ordinary amounts of lime, or with one excessive application, is one of practical, as well as academic significance.

Heiden (30) maintains that $Ca(OH)_2$ remains as such in soil for long periods. Ehrenberg (14) asserts that Heiden's contention is not sustained. It seemed well, therefore, to consider the assumption as unproved, because of Heiden's fallacious reasoning and an effort was made to obtain trustworthy data bearing upon this point. For this purpose there was utilized a field soil which has been limed at frequent intervals during a long period. A soil well adapted to such a study is that of the Pennsylvania Station plats which have received applications of burnt lime semi-annually since 1881. This soil is of limestone origin, and is classified as a silty clay loam of the Hagerstown series. Commencing in 1881, and until very recently, 2 tons of finely ground, unslaked burnt lime were applied each year to each of two plats, numbers 22 and 23, of the tier planted at that time to corn. Recently, however, lime has been slaked prior to its application. Through the courtesy of Prof. C. F. Noll, the writer has had access to the records of the lime plats; while Prof. J. W. White has very kindly furnished freshly taken samples for the analytical work to be described.

Beginning in 1881 and extending through 1915, the following number of pounds of high-grade CaO have been applied to the respective tiers: tier 1, plat 22, 36,500 pounds, plat 23, 36,000 pounds; tier 2, plat 22, 32,500 pounds, plat 23, 36,000 pounds; tier 3, 36,000 pounds for both plats 22 and 23; tier 4, 36,000 pounds, for both plats 22 and 23. The soils of those plats were sampled for analysis in the fall of 1915, 40 borings having been taken from each of the plats of tiers 1, 2 and 3; while 196 borings were secured from each of the two plats of tier 4. The samples used for this study, therefore, represented four series of two plats each. One plat, no. 23, of each pair from the same tier had received lime alone, while the other, no. 22, had received a

supplementary biennial treatment of 6 tons of manure. The four pairs of samples represented respective intervals of less than 1, 2, 3 and 4 years since the application of lime, while the same pairs represented as maximum periods of contact between soil and lime 35, 34, 33 and 32 years, respectively. It should be noted that, even after more than 30 years of cropping, most of the untreated check plats, and many of the fertilized plats, of these tiers were still either slightly alkaline or neutral or else the lime requirement was very low, as indicated by the Veitch method (65). This was shown by Gardner and Brown (24). Hence, it would not be expected that so large a part of the applied lime would be absorbed, in the sense in which the term "absorption" is used as applied to soils, as would be expected if the soil were now distinctively acid or of high lime requirement. However, from ultimate analyses and $CaCO_3$ determinations on these plats in 1911, the writer (47) showed that the increase of $CaCO_3$ from CaO and $Ca(OH)_2$ treatments would not account for the accumulation of calcium. Of the lime remaining in the lime-treated plats, about 35 per cent occurs in forms other than carbonates. Since the same relationship obtained also in the plat treated with ground limestone, it did not at that time seem reasonable to consider the discrepancy between accumulated CaO and the increased $CaCO_3$ content as possibly being due to uncarbonated $Ca(OH)_2$. If only burnt or slaked lime had been applied it might have been assumed that the above-cited data confirmed the contention of Heiden (30) as to the long-continued occurrence of caustic or hydrated lime in soils. Moreover, since the soils contained a large number of pea-sized lumps of lime, it seemed possible that such a contention might be valid, because of possible incomplete carbonation of such lumps. If this were true, pulverization and further exposure would be expected to give an increase in carbonate content. In order to throw light upon this point, the following experiment was carried out. The eight samples from the lime plats were dried in agate ware pans at 105°C. It has already been pointed out that heating to 105°C. had no determinable effect upon the tendency of $Ca(OH)_2$ to revert to the carbonate. All of the dry soil passed through a 2.5-mm. sieve, which, however, stopped a large number of lime lumps. These were added to the soil and the entire sample, amounting in each case to approximately 2 quarts, was then pulverized immediately and passed through a 1-mm. sieve, thoroughly mixed and tightly bottled. Six charges of 25 gm. each were then weighed from each of the eight samples. Each of these charges was then mixed with an equal volume of pure quartz sand and left exposed in shallow tumblers for a period of 3 weeks. In another series, charges of the same weight were placed in 300-cc. Erlenmeyer flasks, which were then filled with moist CO_2 gas and permitted to stand one week, after which time the CO_2 was aspirated off and the samples were again exposed to the atmosphere for a few hours. The two treated series were then analyzed for carbonate CO_2. The analyses, representing from 40 to 60 determinations per series, are given in table 9.

The data of table 9 show that no increase of carbonate resulted after further exposure of the pulverized soil to air, or to an atmosphere of CO_2. This proved conclusively that no $Ca(OH)_2$ was present as residual from either the accumulated earlier applications or the relatively recent ones. The analyses further demonstrate that under the present prevailing conditions in this particular previously heavily limed soil, the carbonation or neutralization of 4000 pounds of CaO per acre was completely effected within a period of 6 months after the application. As supplementing the foregoing tests, one lump of lime weighing about 2.7 gm. was taken from one of the samples of soil and pulverized. A part of the sample was then analyzed in duplicate for CO_2, and another part was treated with carbonated water and

TABLE 9

Complete carbonation of all CaO *added to the Pennsylvania Station plats from 1881 to 1915, inclusive*

TIER	CROP, YEAR OF SAMPLING	PLOT NUMBER	TREATMENT	CALCIUM CARBONATE		
				After grinding, no exposure	After grinding and exposure to atmosphere for 3 weeks	After grinding and exposure to CO_2 for 1 week
				per cent	*per cent*	*per cent*
1	Oats	22	Lime and manure	1.285	1.295	1.295
1	Oats	23	Lime alone	1.173	1.178	1.170
2	Wheat	22	Lime and manure	1.053	1.078	1.074
2	Wheat	23	Line alone	1.515	1.529	1.508
3	Grass	22	Lime and manure	1.335	1.335	1.320
3	Grass	23	Lime alone	1.314	1.313	1.317
4	Corn	22	Lime and manure	1.165	1.164	1.141
4	Corn	23	Lime alone	1.220	1.202	1.203
Average of 40 or more determinations				1.258	1.261	1.254

then analyzed. The percentage of CO_2 in the original portion was found to be identical with that of the CO_2-treated portion. Therefore, in this heavy clay soil containing a large accumulation of lime, no caustic or hydrated lime remained uncarbonated either on the surface or in the soil.

The differences established by the analyses show a lack of uniformity in the composition of the soils of the respective tiers. Furthermore, considering each tier separately, the analytical results in the case of the large plats, adjacent and limed in the same manner, are divergent, in spite of most careful sampling. This fact shows that positive deductions should not be drawn from small differences in the analyses of the soils of these plats in an attempt to demonstrate the effect of burnt lime upon the composition of the soil. Yet smaller analytical differences in the soil of these plats have been

used as the basis of a contention that these plats demonstrate the chemical "burning up" of soil humus and upon such a meagre basis this has been widely taught.

Comparison between the carbonation of $Ca(OH)_2$ *on the surface and when mixed with 1 inch of dry soil*

The first laboratory experiments upon carbonation were for the purpose of studying surface carbonation, as compared to that effected after incorporation of the hydrated lime with dry soil to a depth of 1 inch. The experimental conditions effected were intended to simulate those incident to a surface mulch on the field. It was hoped to determine the speed of carbonation of hydrated lime left on the surface of the dry soil and compared with that taking place when lime is harrowed into the dry soil mulch, which would naturally be relatively inactive as a chemical absorbent. Two alkaline soils were used—a Cumberland brown loam of fair fertility, and a gray residual silt loam of limestone derivation. The Cumberland loam was secured from a spot adjacent to experimental plats of the University of Tennessee Agricultural Experiment Station on the banks of the Tennessee River, near Knoxville. The soil was of alluvial origin, derived partly from a dolomitic limestone. The silty loam was formed *in situ* from Chickamauga limestone and was obtained about six miles from Knoxville, from a tract utilized in coöperative experiments. Nearly two years previously these two soils were used for pot experiments which called for definite applications of $CaCO_3$ in excess of their lime requirement as indicated by the Veitch method (65). The procedure was as follows.

Paraffined paper cartons, 2 inches square and $1\frac{1}{4}$ inches high, were used as containers for charges of soil and lime. Ninety grams of soil, or enough to give 1 inch in depth, were placed in each carton. To each carton, $Ca(OH)_2$ was applied at the rate of 8 tons per surface acre, or 6.1263 gm. per carton. The lime contained 0.82 per cent of CO_2 prior to exposure. In one series the same amount of lime was distributed evenly over the surface of each carton, while in the other admixtures of the entire amounts of lime and soil were made in each carton. All of the cartons were then exposed at the level of the surface soil in a small covered, but well ventilated, outdoor structure. The exposures were made during November and December, 1914. At successive intervals, the soils in the cartons were analyzed. The total weight of the content of each carton was obtained at the time of analysis. The entire content of each carton was then finely ground, and fractions of one-tenth, by weight, were used for analysis. The total gain of CO_2 for each carton was then calculated and correction applied for the CO_2 content of checks. The percentage of carbonation was then determined by comparison with the theoretical amount. The results are embodied in table 10.

The data of table 10 show that the surface applications of hydrated lime reached equilibrium in a short time without complete carbonation having taken place. These layers of lime, about $\frac{3}{16}$ inch in depth, apparently developed protecting coats of $CaCO_3$ around the minute particles of $Ca(OH)_2$, thus delimiting further contact with moisture and CO_2. For, as the data show, a decided increase in carbonation resulted when the applied lime was removed, ground to extreme fineness, and subjected to further exposure.

TABLE 10

Carbonation of $Ca(OH)_2$ *applied to surface of a dry soil and that resulting from its incorporation with 1 inch of the same dry soil*

SOIL	LIME TREATMENT	TIME OF EXPOSURE	CO_2 FOUND	CO_2 INCREASE	CO_2 THEORETICAL TOTAL CARBONATION	CARBONATION	PER ACRE SURFACE
		weeks	*gm.*	*gm.*	*gm.*	*per cent*	*pounds*
Cumberland loam	Spread	1	0.1352	0.1135	0.3635	31.2	4992
	Spread	2	0.2090	0.1872	0.3635	51.5	8240
	Spread	3	0.2130	0.1912	0.3635	52.6	8416
	Spread	4	0.2121	0.1903	0.3635	52.3	8368
	Ground and respread	6	0.2748	0.2497	0.3635	68.7	10992
	Ground and respread	7	0.2768	0.2517	0.3635	69.2	11072
Cumberland loam	Mixed	1	0.0711	0.0493	0.3635	17.4	2784
	Mixed	3	0.1265	0.1047	0.3635	28.8	4608
	Mixed	5	0.2134	0.1916	0.3635	52.7	8432
	Mixed	6	0.2255	0.2004	0.3635	55.1	8816
	Mixed	7	0.2350	0.2099	0.3635	57.7	9232
Silty loam	Spread	1	0.1283	0.1132	0.3635	31.1	4976
	Spread	2	0.2000	0.1848	0.3635	50.8	8128
	Spread	3	0.2026	0.1874	0.3635	51.6	8256
	Spread	4	0.2022	0.1870	0.3635	51.4	8224
	Ground and respread	6	0.2814	0.2629	0.3635	72.1	11536
Silty loam	Mixed	1	0.0557	0.0405	0.3635	11.1	1776
	Mixed	3	0.1309	0.1157	0.3635	31.8	5088
	Mixed	5	0.1984	0.1833	0.3635	50.3	8048
	Mixed	6	0.2112	0.1928	0.3635	52.9	8464
	Mixed	7	0.2295	0.2110	0.3635	57.9	9264

The lime incorporated with the dry soil carbonated more slowly than that applied to the surface. The data indicate that were it deemed desirable to insure complete carbonation of any lumps of $Ca(OH)_2$, prior to its admixture with the soil, it would be advisable to practice dragging, or rolling, or to disturb the surface layer in some such manner. However, the conditions of the experiment were not absolutely comparable with those of the field, in that no moist CO_2-laden soil underlay the treated soil, or rather simulated

soil mulch. Field conditions might result in a greater supply of moisture and CO_2 being made available for carbonation because of diffusion of soil atmosphere. As a matter of fact, such proved to be the case under field conditions. This will later be considered in the light of the data of tables 45,

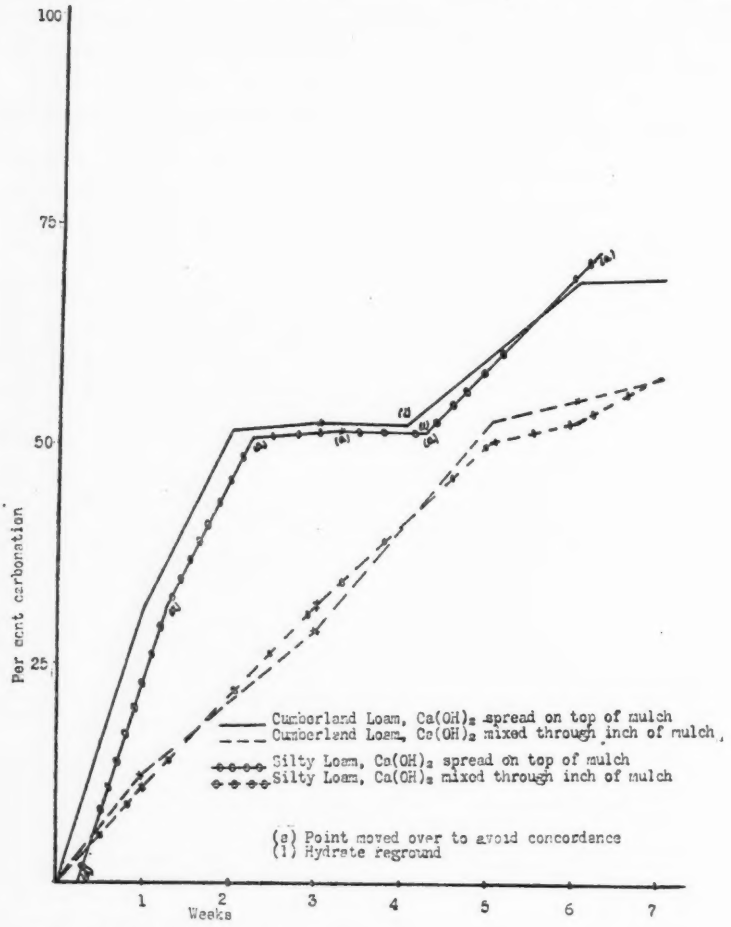

FIG. 1. SURFACE AND INTRA-MULCH EXPOSURES OF $Ca(OH)_2$ (TABLE 10)

46 and 47. While this might affect the speed of the carbonate reaction encountered in both surface and mulch treatments, it would not be expected to change the relationship in the extent of carbonation effected by the two methods of application, surface exposure and incorporation with soil mulch.

Hannen (28) states that diffusion of soil atmosphere is dependent upon size of pores, texture and moisture content. Thus, in the case of sandy and open soils there might be appreciable diffusion of moisture and CO_2 to a layer of lime incorporated in or overlying a dry mulch, while in the case of a fine soil, its absorptive properties, particularly those colloidal, would have a greater retentive influence upon the CO_2. From their studies upon the soil atmosphere, Russell and Appleyard (58) concluded that there exists no close correlation between the changes in soil atmosphere and the aspirating action of winds. In practice, the aspirating effect of wind upon the underlying moist and CO_2-laden soil would be very probably minimized by the presence of a mulch, such as was simulated by the use of the dry soil in the preceding experiment.

FIELD CYLINDER STUDIES

The first field study involved comparisons between carbonation resulting from chemically equivalent amounts of CaO and $Ca(OH)_2$, mixed throughout an acid loam soil. The soil utilized in this experiment was the brown loam used in the preceding mulch exposure experiment and previously described. The preliminary studies of tables 1 to 8 show, however, that the oxide would quickly derive from the soil the moisture essential for hydration. Hence, it is probable that the use of the burnt oxide was simply equivalent to increasing the number of $Ca(OH)_2$ treatments included in the study. On the other hand, in the preliminary studies, wherein the oxide and hydrate were exposed at the same time and place, it was shown that the probable simultaneous taking up of H_2O and CO_2 by the oxide resulted in a more rapid conversion to carbonate, than was effected by the hydrate where only the absorption of CO_2 was essential to the formation of carbonate.

Chemical equivalence of CaO, $Ca(OH)_2$ and $CaCO_3$ treatments was determined by dissolving each of the substances in an excess of acid and titrating back the excess. Chemically equivalent amounts of pure precipitated $CaCO_3$ were used as checks. All materials applied were weighed and sealed in bottles in the laboratory. They were opened immediately before mixing with the soils of the field cylinders. The treatments were based upon equivalence of 4,000 pounds and 16,000 pounds of CaO per acre 2,000,000 pounds of soil, approximating 8 inches in depth. Some of the CaO treatments were unsupplemented, while others received supplementary treatments of finely chopped dry barnyard manure at the rate of 12, 30 and 48 tons per acre 2,000,000 pounds of soil. The burnt lime used was approximately 97 per cent CaO, and had been recently burned. The hydrated lime was obtained by the water-slaking of the same burnt lime. Related studies to determine the difference between the ability of the soil to effect the decomposition of ground limestone, as compared to its ability to decompose the more finely divided precipitated $CaCO_3$, demonstrated that the latter form should be used as a check in determining the conversion of the applied lime and hydrate to the carbonate.

In the entire experiment, of which the carbonation studies were but a part, about 15 tons of $\frac{1}{4}$-inch-screened and thoroughly mixed soil were handled. The preliminary mixing was done by 9 men working in a circle around the soil heap. When the laboratory sample was air-dried, approximately 97 per cent passed through a 0.5-mm. sieve.

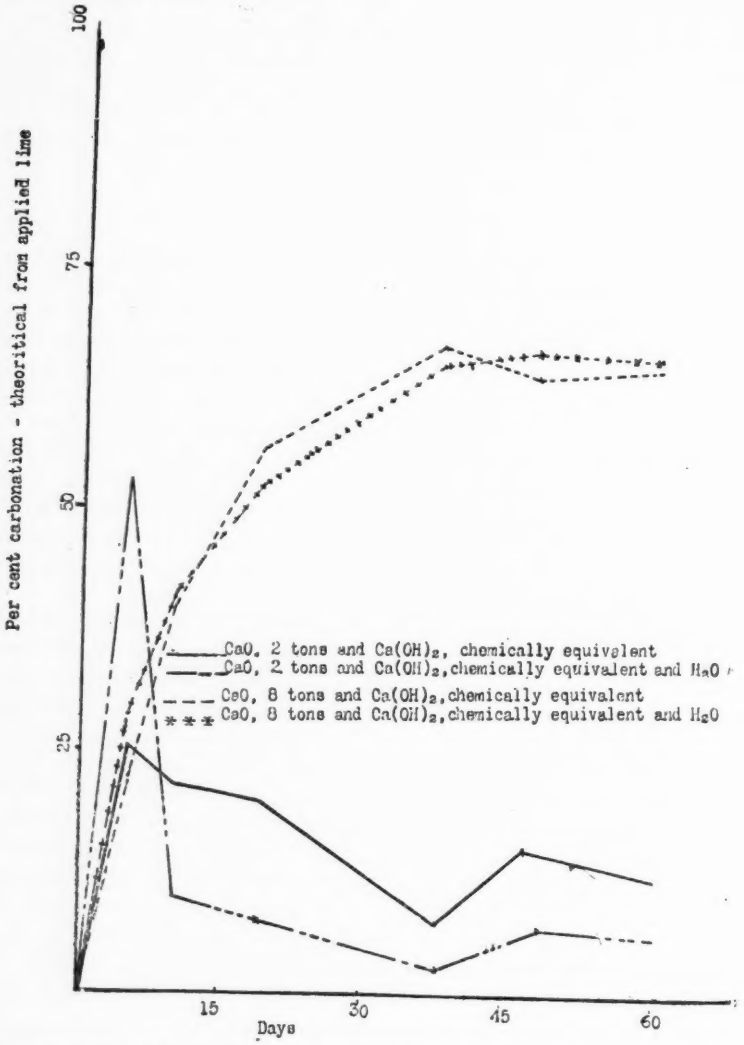

FIG. 2. SPEED OF CARBONATION OF THE CaO AND $Ca(OH)_2$ APPLIED TO ACID CUMBERLAND LOAM IN THE CYLINDERS (TABLES 11 TO 20)

Cloudy, misty weather prevailed during the handling of the soil, and its transfer from a nearby source to cylinders was accomplished without any determinable change in moisture. There was approximately 15 per cent of moisture in the soil at the time of placing and treatment.

The cylinders used as containers for the treated soil were 12 inches in depth and embraced an area of 1/10,000 acre. They were part of a set comprising a total number of 128. Each cylinder received enough moist soil to furnish 200 pounds of moisture-free soil. This was placed as follows: In each cylinder was first placed, untreated, one-fourth of the total amount to be placed, equivalent to 50 pounds of moisture-free soil. This rested upon the

TABLE 11

A field cylinder study of the carbonation of CaO *when applied at the rate of 2 tons per acre, 8 inches, and immediately mixed throughout the upper 6 inches of a moist acid Cumberland loam soil*

LABORATORY NUMBER	CYLINDER NUMBER	NUMBER OF DAYS BETWEEN TREATMENT AND SAMPLING	TREATMENT OTHER THAN LIME	MOISTURE AT TIME OF SAMPLING	CO_2 IN WET SOIL	CO_2 IN MOISTURE-FREE SOIL	CO_2 IN BLANK MOISTURE-FREE SOIL	INCREASE IN CO_2 IN MOISTURE-FREE SOIL FROM TREATMENT	INCREASE PER ACRE 2,000,000 POUNDS OF SOIL CALCULATED AS		INCREASE OF $CaCO_3$ PER CENT OF THEORY FROM APPLIED CaO
									CO_2	$CaCO_3$	
				per cent	*per cent*	*per cent*	*per cent*	*per cent*	*lbs.*	*lbs.*	*per cent*
2540	L1	5	No H_2O	11.95	0.0592	0.0673	0.0334	0.0339	678	1541	21.9
2566	L1	10	No H_2O	11.30	0.0618	0.0694	0.0336	0.0358	716	1627	23.1
2610	L1	19	No H_2O	10.75	0.0406	0.0455	0.0044	0.0411	822	1868	26.5
2636	L1	38	No H_2O	11.64	0.0188	0.0213	0.0134	0.0079	158	359	5.1
2662	L1	47	No H_2O	11.49	0.0430	0.0486	0.0243	0.0243	486	1104	15.8
2692	L1	61	No H_2O	10.54	0.0449	0.0502	0.0290	0.0290	424	964	13.7
2553	M1	5	H_2O added	13.90	0.0848	0.0985	0.0061	0.0924	1848	4200	59.9
2587	M1	10	H_2O added	14.30	0.0218	0.0254	0.0160	0.0094	188	427	6.1
2623	M1	19	H_2O added	12.53	0.0184	0.0210	0.0104	0.0106	212	482	6.8
2649	M1	38	H_2O added	14.05	0.0100	0.0116	0.0171	0.0000	000	000	0.0
2677	M1	47	H_2O added	14.50	0.0284	0.0321	0.0290	0.0031	62	141	2.0
2708	M1	61	H_2O added	14.65	0.0307	0.0360	0.0333	0.0027	54	123	1.7

native undisturbed red clay subsoil and it was intended that it should serve as a buffer, in case of any leaching during the period of experimentation. Each treatment was then mixed with the upper 6 inches of moist soil, equivalent to 150 pounds of moisture-free soil. The soil and treatments were mixed in metal lined boxes. Two men were assigned to each box and hoes were used to accomplish thorough mixing The treated soil was then placed in the cylinders and gently tamped.

At the beginning of the experiment it was thought well to consider the influence of varying soil moisture upon the rate of carbonation. Consequently, immediately after placing, one series was further moistened by the

addition of an inch of river water, applied evenly to the soil by the aid of a cheese-cloth covering. The other set was not further treated. During the 8-week period covered by the experiment, a total application of 8 inches of water supplemented the light natural rainfall and this was evenly distributed,

TABLE 12

A field-cylinder study of the carbonation of CaO *when applied at the rate of 2 tons per acre 8 inches together with dry barnyard manure and both substances immediately mixed throughout the upper 6 inches of a moist acid Cumberland loam soil*

LABORATORY NUMBER	CYLINDER NUMBER	NUMBER OF DAYS BETWEEN TREATMENT AND SAMPLING	TREATMENT OTHER THAN LIME	MOISTURE AT TIME OF SAMPLING	CO_2 IN WET SOIL	CO_2 IN MOISTURE-FREE SOIL	CO_2 IN BLANK MOISTURE-FREE SOIL	INCREASE IN CO_2 IN MOISTURE-FREE SOIL FROM TREATMENT	INCREASE PER ACRE 2,000,000 POUNDS OF SOIL CALCULATED AS		INCREASE OF $CaCO_3$ PER CENT OF THEORY FROM APPLIED CaO
									CO_2	$CaCO_3$	
				per cent	*per cent*	*per cent*	*per cent*	*per cent*	*lbs.*	*lbs.*	*per cent*
2542	L7	5	12 T. manure, no H_2O	11.10	0.0688	0.0774	0.0334	0.0440	884	2000	28.4
2568	L7	10	12 T. manure, no H_2O	11.23	0.0588	0.0662	0.0336	0.0326	652	1482	21.3
2612	L7	19	12 T. manure, no H_2O	10.80	0.0343	0.0385	0.0044	0.0341	682	1550	22.0.
2638	L7	38	12 T. manure, no H_2O	12.83	0.0220	0.0252	0.0134	0.0118	236	536	7.6
2665	L7	47	12 T. manure, no H_2O	12.23	0.0438	0.0499	0.0243	0.0256	512	1164	16.5
2695	L7	61	12 T. manure, no H_2O	10.51	0.0465	0.0520	0.0290	0.0230	460	1045	14.8
2555	M7	5	12 T. manure, and H_2O	14.80	0.0728	0.0854	0.0061	0.0793	1586	3604	51.1
2589	M7	10	12 T. manure, and H_2O	14.81	0.0267	0.0314	0.0160	0.0154	308	700	9.9
2625	M7	19	12 T. manure, and H_2O	12.00	0.0162	0.0184	0.0104	0.0080	160	364	5.1
2651	M7	38	12 T. manure, and H_2O	14.63	0.0162	0.0190	0.0171	0.0019	38	86	1.2
2680	M7	47	12 T. manure, and H_2O	15.66	0.0320	0.0379	0.0290	0.0089	178	404	5.7
2711	M7	61	12 T. manure, and H_2O	16.16	0.0375	0.0442	0.0333	0.0109	218	495	7.0

in order to prevent leaching. The treated soils were placed June 11, 1913, and were sampled at successive intervals of 5, 10, 19, 38, 47 and 61 days thereafter. The samples were collected for the full 8-inch depth to the clay subsoil and immediately bottled and transported to the laboratory where they were passed through a 2-mm. sieve, mixed and at once analyzed in the

moist condition for CO_2. The butter-sampler holes made in taking samples were immediately filled. The original soil was acid to litmus and was practically carbonate-free. The CO_2 obtained by its analysis might be considered on the whole as negligible and as well within laboratory error. With the moist unground acid soils, however, even after preliminary treatment for long periods with dilute HCl, there is always a slight CO_2 evolution due probably to action of acid upon soil organic matter or to residual traces of CO_2 condensed upon the surface of the soil particles. This small analytical

TABLE 13

A field-cylinder study of the carbonation of CaO *when applied at the rate of 2 tons per acre 8 inches together with dry barnyard manure and both substances immediately mixed throughout the upper 6 inches of a moist acid Cumberland loam soil*

LABORATORY NUMBER	CYLINDER NUMBER	NUMBER OF DAYS BETWEEN TREATMENT AND SAMPLING	TREATMENT OTHER THAN LIME	MOISTURE AT TIME OF SAMPLING	CO_2 IN WET SOIL	CO_2 IN MOISTURE-FREE SOIL	CO_2 IN BLANK MOISTURE-FREE SOIL	INCREASE IN CO_2 IN MOISTURE-FREE SOIL FROM TREATMENT	INCREASE PER ACRE 2,000,000 POUNDS OF SOIL CALCULATED AS		INCREASE OF $CaCO_3$ PER CENT OF THEORY FROM APPLIED CaO
									CO_2	$CaCO_3$	
				per cent	*per cent*	*per cent*	*per cent*	*per cent*	*lbs.*	*lbs.*	*per cent*
2545	L13	5	30 T. manure, no H_2O	11.28	0.0504	0.0568	0.0355	0.0213	426	968	13.7
2574	L13	10	30 T. manure, no H_2O	11.30	0.0558	0.0629	0.0170	0.0457	914	207	28.1
2615	L13	19	30 T. manure, no H_2O	10.69	0.0408	0.0457	0.0041	0.0416	832	1891	26.8
2641	L13	38	30 T. manure, no H_2O	13.87	0.0339	0.0394	0.0258	0.0136	276	627	8.9
2668	L13	47	30 T. manure, no H_2O	13.90	0.0452	0.0525	0.0316	0.0209	418	950	13.5
2698	L13	61	30 T. manure, no H_2O	11.18	0.0446	0.0502	0.0316	0.0186	372	845	12.0
2558	M13	5	30 T. manure, and H_2O	14.70	0.1026	0.1203	0.0563	0.0640	1280	2909	41.3
2595	M13	10	30 T. manure, and H_2O	15.16	0.0226	0.0266	0.0039	0.0227	454	1032	14.6
2628	M13	19	30 T. manure, and H_2O	12.42	0.0194	0.0222	0.0020	0.0202	404	918	13.0
2654	M13	38	30 T. manure, and H_2O	15.78	0.0258	0.0306	0.0293	0.0013	26	59	0.8
2683	M13	47	30 T. manure, and H_2O	16.00	0.0364	0.0433	0.0261	0.0172	344	782	11.1
2714	M13	61	30 T. manure, and H_2O	15.94	0.0388	0.0462	0.0309	0.0153	306	695	9.9

error was, therefore, considered and blanks were run with each set of analyses. This point will be considered further by the consideration of experimental errors, as indicated by the data of table 22. In addition several attempts were made, without success, to determine any difference between the carbonate blank of untreated soil and that of the 6-ton manure treatments.

The increases of CO_2 resulting from carbonation of lime applied are given in tables 11 to 21, inclusive.

Discussion of speed of carbonation as determined from field cylinder studies

Two tons CaO *without water.* The lighter treatments of CaO without applications of water will be considered first.

Inspection of tables 11, 12 and 13 indicates a very slight but consistently greater apparent carbonate CO_2 content in the cylinders to which CaO was applied at the rate of 2 tons per acre, as compared to the cylinders receiving no lime. The small analytical differences, however, when converted into pounds per acre represent appreciable quantities, apparent or real The

TABLE 14

A field cylinder study of the carbonation of $Ca(OH)_2$ *when applied at the rate of 2 tons of* CaO *per acre 8 inches and immediately mixed throughout the upper 6 inches of the moist acid Cumberland loam soil*

LABORATORY NUMBER	CYLINDER NUMBER	NUMBER OF DAYS BETWEEN TREATMENT AND SAMPLING	TREATMENT OTHER THAN LIME	MOISTURE AT TIME OF SAMPLING	CO_2 IN WET SOIL	CO_2 IN MOISTURE-FREE SOIL	CO_2 IN BLANK MOISTURE-FREE SOIL	INCREASE IN CO_2 IN MOISTURE-FREE SOIL FROM TREATMENT	INCREASE PER ACRE 2,000,000 POUNDS OF SOIL CALCULATED AS		INCREASE OF $CaCO_3$ PER CENT OF THEORY FROM APPLIED $Ca(OH)_2$
									CO_2	$CaCO_3$	
				per cent	*per cent*	*per cent*	*per cent*	*per cent*	*lbs.*	*lbs.*	*per cent*
2541	L2	5	No H_2O	11.76	0.0760	0.0861	0.0334	0.0527	1054	2395	34.0
2567	L2	10	No H_2O	10.98	0.0618	0.0694	0.0336	0.0358	716	1627	23.1
2611	L2	19	No H_2O	10.44	0.0318	0.0355	0.0044	0.0311	622	1414	20.1
2637	L2	38	No H_2O	12.21	0.0225	0.0256	0.0134	0.0122	244	554	7.9
2663	L2	47	No H_2O	12.07	0.0325	0.0370	0.0243	0.0127	254	577	8.2
2693	L2	61	No H_2O	10.37	0.0379	0.0423	0.0290	0.0133	266	604	8.6
2554	M2	5	H_2O applied	14.20	0.0744	0.0867	0.0061	0.0806	1612	3664	52.0
2588	M2	10	H_2O applied	14.31	0.0264	0.0308	0.0160	0.0148	296	673	9.6
2624	M2	19	H_2O applied	11.92	0.0136	0.0154	0.0104	0.0050	100	227	3.2
2650	M2	38	H_2O applied	14.25	0.0268	0.0313	0.0171	0.0142	284	645	9.2
2678	M2	47	H_2O applied	15.32	0.0276	0.0326	0.0290	0.0036	72	164	2.3
2709	M2	61	H_2O applied	14.93	0.0344	0.0404	0.0333	0.0071	142	323	4.5

close agreement between the results of the first three samplings at the end of 5, 10 and 19 days, respectively, show that maximum carbonation ensued during the interval of 5 days between treatment and the first sampling. The carbonation of the lime not directly absorbed by the soil was apparently effected in large part by the initial CO_2 content of the moist soil. It is possible that the lime produced an acceleration in the generation of CO_2, thereby supplementing the initial supply available to effect carbonation. However, there appears to have been no acceleration in the rate of carbonation as a result of the simultaneous incorporation of dry organic matter, during the first three periods. This is not at all in harmony with what would

be anticipated from the results given by Fraps (18), who reported very extensive decompositions of various kinds of organic matter within 3 days after its contact with soil. However, in Fraps' studies 23 of the 25 soils studied were of sandy types and no caustic lime was added. The biological

TABLE 15

A field-cylinder study of the carbonation of $Ca(OH)_2$ *when applied at the rate of 2 tons per acre 8 inches together with dry barnyard manure and both substances immediately mixed throughout the upper 6 inches of a moist acid Cumberland loam soil*

LABORATORY NUMBER	CYLINDER NUMBER	NUMBER OF DAYS BETWEEN TREATMENT AND SAMPLING	TREATMENT OTHER THAN LIME	MOISTURE AT TIME OF SAMPLING	CO_2 IN WET SOIL	CO_2 IN MOISTURE-FREE SOIL	CO_2 IN BLANK MOISTURE-FREE SOIL	INCREASE IN CO_2 IN MOISTURE-FREE SOIL FROM TREATMENT	INCREASE PER ACRE 2,000,000 POUNDS OF SOIL CALCULATED AS		INCREASE OF $CaCO_3$ PER CENT OF THEORY FROM APPLIED $Ca(OH)_2$
									CO_2	$CaCO_3$	
				per cent	*per cent*	*per cent*	*per cent*	*per cent*	*lbs.*	*lbs.*	*per cent*
2543	L8	5	12 T. manure, no H_2O	11.83	0.0808	0.0916	0.0334	0.0682	1364	3100	44.0
2569	L8	10	12 T. manure, no H_2O	10.84	0.0540	0.0606	0.0336	0.0270	540	1227	17.4
2613	L8	19	12 T. manure, no H_2O	10.69	0.0284	0.0318	0.0044	0.0274	548	1245	17.7
2639	L8	38	12 T. manure, no H_2O	11.18	0.0202	0.0227	0.0134	0.0093	186	423	6.0
2666	L8	47	12 T. manure, no H_2O	12.14	0.0388	0.0442	0.0243	0.0199	398	904	12.8
2696	L8	61	12 T. manure, no H_2O	10.50	0.0432	0.0483	0.0290	0.0193	386	877	12.4
2556	M8	5	12 T. manure, and H_2O	14.70	0.0892	0.1045	0.0061	0.0984	1968	4454	63.2
2590	M8	10	12 T. manure, and H_2O	14.58	0.0271	0.0317	0.0160	0.0157	314	714	10.1
2626	M8	19	12 T. manure, and H_2O	11.72	0.0186	0.0211	0.0104	0.0107	214	486	6.9
2652	M8	38	12 T. manure, and H_2O	15.25	0.0144	0.0170	0.0171	0.0000	000	000	0.0
2681	M8	47	12 T. manure, and H_1O	15.60	0.0354	0.0419	0.0290	0.0129	258	586	8.3
2712	M8	61	12 T. manure, and H_2O	15.52	0.0380	0.0450	0.0333	0.0117	234	554	7.8

studies of Hutchinson (37, 38) would suggest the probability of a marked acceleration of bacterial activities and an absence of partial sterilizing effect from this light treatment of lime The analyses of the same cylinders at the latter three periods of contact, 38, 47 and 61 days, shows a consistent decrease

in the amount of $CaCO_3$. These data point to direct absorption by the soil of a considerable part of the CaO followed by a carbonation of the fraction not immediately absorbed. Further absorption by the soil of that portion of the lime which underwent carbonation then ensued. It is possible, how-

TABLE 16

A field-cylinder study of the carbonation of $Ca(OH)_2$ *when applied at the rate of 2 tons of* CaO *per acre 8 inches together with dry barnyard manure and both substances immediately mixed throughout the upper 6 inches of a moist acid Cumberland loam soil*

LABORATORY NUMBER	CYLINDER NUMBER	NUMBER OF DAYS BETWEEN TREATMENT AND SAMPLING	TREATMENT OTHER THAN LIME	MOISTURE AT TIME OF SAMPLING	CO_2 IN WET SOIL	CO_2 IN MOISTURE-FREE SOIL	CO_2 IN BLANK MOISTURE-FREE SOIL	INCREASE IN CO_2 IN MOISTURE-FREE SOIL FROM TREATMENT	INCREASE PER ACRE 2,000,000 POUNDS OF SOIL CALCULATED AS		INCREASE OF CaO_2 PER CENT OF THEORY FROM APPLIED $Ca(OH)_2$
									CO_2	$CaCO_3$	
				per cent	*per cent*	*per cent*	*per cent*	*per cent*	*lbs.*	*lbs.*	*per cent*
2546	L14	5	30 T. manure, no H_2O	11.70	0.0506	0.0573	0.0355	0.0218	436	991	12.6
2575	L14	10	30 T. manure, no H_2O	10.98	0.0398	0.0447	0.0170	0.0277	554	1282	18.2
2616	L14	19	30 T. manure, no H_2O	10.62	0.0300	0.0336	0.0041	0.0295	590	1341	19.0
2642	L14	38	30 T. manure, no H_2O	14.50	0.0341	0.0399	0.0258	0.0141	282	641	9.1
2669	L14	47	30 T. manure, no H_2O	13.54	0.0546	0.0632	0.0316	0.0316	732	1664	23.6
2699	L14	61	30 T. manure, no H_2O	11.63	0.0430	0.0487	0.0316	0.0171	342	777	11.0
2559	M14	5	30 T. manure, and H_2O	14.60	0.0546	0.0639	0.0563	0.0076	152	345	4.9
2596	M14	10	30 T. manure, and H_2O	15.30	0.0176	0.0208	0.0039	0.0169	338	768	10.9
2629	M14	19	30 T. manure, and H_2O	12.30	0.0162	0.0185	0.0020	0.0165	330	750	10.6
2655	M14	38	30 T. manure, and H_2O	13.52	0.0322	0.0372	0.0293	0.0079	158	359	5.9
2684	M14	47	30 T. manure, and H_2O	10.05	0.0411	0.0457	0.0261	0.0196	392	891	12.6
2715	M14	61	30 T. manure, and H_2O	16.10	0.0372	0.0443	0.0309	0.0134	268	509	7.2

ever, that carbonation preceded absorption, i.e., that the lime absorbed by the soil during the first interval of 5 days may have been derived largely from the form of $CaCO_3$, to which compound the CaO may have been converted subsequent to its hydration and solution by the soil moisture. It seems

definitely established, however, that maximum carbonation ensued within 5 days, whereas the maximum of measurable absorption did not occur until between 10 to 19 days after treatment. In the summation of the data from the twelve 2-ton cylinders, this fact will be further discussed.

Two tons of CaO *plus water.* Considering next the cylinders treated in like manner as to amount of CaO and manure, but with additions of water, the data of tables 11, 12 and 13 show a marked variation in the rate of carbonation effected. In each case the maximum carbonation is indicated at the end of the first interval of 5 days. Beyond that period, the decrease in car-

TABLE 17

A field-cylinder study of the carbonation of CaO *when applied at the rate of 8 tons per acre 8 inches and immediately mixed throughout the upper 6 inches of a moist acid Cumberland loam soil*

LABORATORY NUMBER	CYLINDER NUMBER	NUMBER OF DAYS BETWEEN TREATMENT AND SAMPLING	TREATMENT OTHER THAN LIME	MOISTURE AT TIME OF SAMPLING	CO_2 IN WET SOIL	CO_2 IN MOISTURE-FREE SOIL	CO_2 IN BLANK MOISTURE-FREE SOIL	INCREASE IN CO_2 IN MOISTURE-FREE SOIL FROM TREATMENT	INCREASE PER ACRE 2,000,000 POUNDS OF SOIL CALCULATED AS		INCREASE OF $CaCO_3$ PER CENT OF THEORY FROM APPLIED CaO
									CO_2	$CaCO_3$	
				per cent	*per cent*	*per cent*	*per cent*	*per cent*	*lbs.*	*lbs.*	*per cent*
2551	L25	5	No H_2O	11.19	0.1280	0.1441	0.0334	0.1107	2214	5,032	17.9
2585	L25	10	No H_2O	7.37	0.3184	0.3437	0.0336	0.3101	6202	14,095	50.0
2621	L25	19	No H_2O	10.33	0.3678	0.4102	0.0044	0.4058	8116	18,432	65.4
2647	L25	38	No H_2O	11.60	0.3814	0.4315	0.0134	0.4181	8362	19,004	67.4
2674	L25	47	No H_2O	11.56	0.3812	0.4310	0.0243	0.4067	8134	18,486	65.6
2704	L25	61	No H_2O	10.38	0.3922	0.4376	0.0290	0.4086	8172	18,572	65.9
2564	M25	5	H_2O applied	14.60	0.1863	0.2182	0.0266	0.1916	3832	8,709	30.9
2606	M25	10	H_2O applied	12.39	0.2443	0.2789	0.0160	0.2629	5258	11,950	42.4
2634	M25	19	H_2O applied	12.68	0.2316	0.2652	0.0104	0.2548	5096	11,582	41.1
2660	M25	38	H_2O applied	15.70	0.3530	0.4188	0.0171	0.4017	8034	18,259	64.8
2689	M25	47	H_2O applied	15.53	0.3722	0.4404	0.0290	0.4114	8228	18,700	66.4
2720	M25	61	H_2O applied	16.63	0.3892	0.4612	0.0333	0.4279	8558	19,450	69.0

bonates is very marked. It is possible that the water added resulted in a marked and immediate increase in biological activities, thus causing a speedy carbonation followed by more thorough diffusion of dissolved $CaCO_3$ and hence greater absorption. In these cylinders it appears that maximum carbonation and minimum absorption occurred at a much earlier period than the 10 to 19 days' interval required by the unwetted cylinders.

The data derived from the six wetted cylinders demonstrate beyond doubt that complete carbonation ensued uniformly within the period of 5 days. In these cylinders the abundance of moisture available to permeate

the very fine lime particles very probably prevented the protective action of $CaCO_3$ crusts and the attaining of apparent equilibrium before complete carbonation was actually effected, differing in this manner from the case of dry mulch results of table 10.

TABLE 18

A field-cylinder study of the carbonation of CaO *when applied at the rate of 8 tons of* CaO *per acre 8 inches together with dry barnyard manure and both substances immediately mixed throughout the upper 6 inches of a moist acid Cumberland loam soil*

LABORATORY NUMBER	CYLINDER NUMBER	NUMBER OF DAYS BETWEEN TREATMENT AND SAMPLING	TREATMENT OTHER THAN LIME	MOISTURE AT TIME OF SAMPLING	CO_2 IN WET SOIL	CO_2 IN MOISTURE-FREE SOIL	CO_2 IN BLANK MOISTURE-FREE SOIL	INCREASE IN CO_2 in MOISTURE-FREE SOIL FROM TREATMENT	INCREASE PER ACRE 2,000,000 POUNDS OF SOIL CALCULATED AS		INCREASE OF $CaCO_3$ PER CENT OF THEORY FROM APPLIED $Ca(OH)_2$
									CO_2	$CaCO_3$	
				per cent	*per cent*	*per cent*	*per cent*	*per cent*	*lbs.*	*lbs.*	*per cen*
2548	L19	5	48 T. manure, no H_2O	11.29	0.1408	0.1587	0.0107	0.1480	2960	6,727	23.9
2580	L19	10	48 T. manure, no H_2O	10.71	0.2136	0.2392	0.0187	0.2205	4410	10,023	35.5
2618	L19	19	48 T. manure, no H_2O	10.49	0.3264	0.3647	0.0075	0.3572	7144	14,288	56.7
2644	L19	38	48 T. manure, no H_2O	12.62	0.4170	0.4772	0.0264	0.4508	9016	18,032	64.0
2671	L19	47	48 T. manure, no H_2O	12.67	0.3952	0.4525	0.0313	0.4212	8424	16,848	59.8
2701	L19	61	48 T. manure, no H_2O	10.69	0.4076	0.4564	0.0318	0.4246	8492	16,984	60.3
2561	M19	5	48 T. manure, and H_2O	14.40	0.1584	0.1850	0.0310	0.1540	3080	6,160	21.9
2601	M19	10	48 T. manure, and H_2O	15.32	0.2150	0.2539	0.0135	0.2404	4808	9,616	34.1
2631	M19	19	48 T. manure, and H_2O	12.72	0.3670	0.4205	0.0038	0.4167	8334	16,668	59.1
2657	M19	38	48 T. manure, and H_2O	16.47	0.3792	0.4540	0.0286	0.4254	8508	17,016	60.4
2686	M19	47	48 T. manure, and H_2O	16.03	0.3982	0.4741	0.0276	0.4465	8930	17,860	63.4
2717	M19	61	48 T. manure, and H_2O	15.98	0.3730	0.4440	0.0325	0.4115	8230	16,460	58.4

Two tons of CaO *as* $Ca(OH)_2$, *without water.* Coming next to the consideration of 2-ton treatments of CaO, when applied as $Ca(OH)_2$ without addition of water, we find no marked difference between the activities of the hydrate, as compared to the oxide. This would be expected for the CaO would

quickly combine with soil moisture giving $Ca(OH)_2$ and in effect, producing identical treatments. Cylinders 12 and 18 show, as do their corresponding cylinders receiving CaO, that maximum carbonation ensued within 5 days while the difference indicated by the analysis as occurring in cylinder 14 between the 5- and 10-day interval is hardly sufficient to justify the statement that, in this case, maximum carbonation was delayed until the 10-day interval. As a matter of fact, however, the corresponding cylinders L13 and L14 exhibit somewhat the same tendency, if the small analytical differences are considered as sufficiently positive to register such retardation.

TABLE 19

A field-cylinder study of the carbonation of $Ca(OH)_2$ *when applied at the rate of 8 tons of* CaO *per acre 8 inches and immediately mixed throughout the upper 6 inches of a moist acid Cumberland loam soil*

LABORATORY NUMBER	CYLINDER NUMBER	NUMBER OF DAYS BETWEEN TREATMENT AND SAMPLING	TREATMENT OTHER THAN LIME	MOISTURE AT TIME OF SAMPLING	CO_2 IN WET SOIL	CO_2 IN MOISTURE-FREE SOIL	CO_2 IN BLANK MOISTURE-FREE SOIL	INCREASE IN CO_2 IN MOISTURE-FREE SOIL FROM TREATMENT	INCREASE PER ACRE 2,000,000 POUNDS OF SOIL CALCULATED AS		INCREASE OF $CaCO_3$ PER CENT OF THEORY FROM APPLIED $Ca(OH)_2$
									CO_2	$CaCO_3$	
				per cent	*per cent*	*per cent*	*per cent*	*per cent*	*lbs.*	*lbs.*	*per cent*
2552	L26	5	No H_2O	11.20	0.1376	0.1550	0.0334	0.1216	2432	5,527	19.5
2585	L26	10	No H_2O	8.22	0.2626	0.2861	0.0336	0.2525	5050	11,477	40.7
2622	L26	19	No H_2O	9.85	0.2614	0.2900	0.0044	0.2856	5712	12,982	46.1
2648	L26	38	No H_2O	11.87	0.3754	0.4259	0.0134	0.4125	8250	18,704	66.3
2675	L26	47	No H_2O	8.47	0.3900	0.4261	0.0243	0.4018	8036	18,241	64.7
2705	L26	61	No H_2O	12.23	0.3844	0.4380	0.0290	0.4090	8180	18,591	66.0
2565	M26	5	H_2O applied	15.00	0.1782	0.2096	0.0061	0.2035	4070	9,250	32.8
2606	M26	10	H_2O applied	10.94	0.3026	0.3360	0.0160	0.3200	6400	14,545	51.5
2635	M26	19	H_2O applied	12.92	0.2504	0.2876	0.0104	0.2772	5544	12,600	44.7
2661	M26	38	H_2O applied	16.22	0.3594	0.4290	0.0171	0.4119	8238	18,704	67.1
2690	M26	47	H_2O applied	15.54	0.3858	0.4568	0.0290	0.4278	8556	19,432	68.9
2721	M26	61	H_2O applied	15.72	0.3722	0.4415	0.0333	0.4082	8164	18,554	65.8

Two tons of CaO, *as* $Ca(OH)_2$, *plus water.* Duplication of the above treatments was also effected with additions of water. From the data of tables 14, 15 and 16 it appears that the cylinders receiving no manure and the smaller applications of manure attained maximum carbonation within 5 days, as did their corresponding CaO-treated cylinders, while maximum immediate absorption had been practically effected by the end of the 10-day period. However, where the heavy manure treatment was applied, maximum absorption and maximum carbonation seemed to be coincident.

It should be borne in mind that the analyses of cylinders were carried out upon moist soils. These soils were analyzed the same day as sampled, first

being run through a 2-mm. sieve and mixed. In this way, the soil moisture was devoid of increased pressure and its structure was so disintegrated as to induce diffusion of soil atmosphere to the air. No differences could be detected between the CO_2 liberated by acid from the moist check soils thus

TABLE 20

A field-cylinder study of the carbonation of $Ca(OH)_2$ *when applied at the rate of 8 tons of* CaO *per acre 8 inches together with dry barnyard manure and both substances immediately mixed throughout the upper 6 inches of moist acid Cumberland loam soil*

LABORATORY NUMBER	CYLINDER NUMBER	NUMBER OF DAYS BETWEEN TREATMENT AND SAMPLING	TREATMENT OTHER THAN LIME	MOISTURE AT TIME OF SAMPLING	CO_2 IN WET SOIL	CO_2 IN MOISTURE-FREE SOIL	CO_2 IN BLANK MOISTURE-FREE SOIL	INCREASE IN CO_2 IN MOISTURE-FREE SOIL FROM TREATMENT	INCREASE PER ACRE 2,000,000 POUNDS OF SOIL CALCULATED AS		INCREASE OF $CaCO_3$ PER CENT OF THEORY FROM APPLIED $Ca(OH)_2$
									CO_2	$CaCO_3$	
				per cent	*per cent*	*per cent*	*per cent*	*per cent*	*lbs.*	*lbs*	*per cent*
2549	L20	5	48 T. manure, no H_2O	11.21	0.1416	0.1595	0.0107	0.1488	2976	6,764	24.0
2581	L20	10	48 T. manure, no H_2O	11.42	0.2010	0.2271	0.0187	0.2084	4168	9,473	33.6
2619	L20	19	48 T. manure, no H_2O	10.27	0.3266	0.3640	0.0075	0.3565	7130	16,204	57.5
2645	L20	38	48 T. manure, no H_2O	12.30	0.4326	0.4933	0.0264	0.4669	9338	21,223	75.3
2672	L20	47	48 T. manure, no H_2O	11.56	0.4074	0.4607	0.0313	0.4294	8588	19,518	65.7
2702	L20	61	48 T. manure, no H_2O	12.00	0.4002	0.4547	0.0318	0.4229	8458	19,277	68.4
2562	M20	5	48 T. manure, and H_2O	14.50	0.1816	0.2124	0.0310	0.1814	3628	8,245	29.3
2602	M20	10	48 T. manure, and H_2O	15.27	0.2150	0.2538	0.0135	0.2383	4766	10,363	36.7
2632	M20	19	48 T. manure, and H_2O	13.46	0.3552	0.4105	0.0038	0.4067	8134	18,486	65.6
2658	M20	38	48 T. manure, and H_2O	16.27	0.3980	0.4754	0.0286	0.4468	8936	20,309	72.1
2687	M20	47	48 T. manure, and H_2O	14.13	0.4058	0.4726	0.0276	0.4450	8900	20,227	71.8
2718	M20	61	48 T. manure, and H_2O	16.18	0.3944	0.4706	0.0325	0.4381	8762	19,914	70.6

treated and that obtained from the same soils after air-drying, by most careful manipulation. Theoretically, however, it might be assumed that in the fresh soil, part of the determined CO_2 was to be attributed to possible gaseous CO_2 from accelerated biological activities, in case all of the lime

had been carbonated. Comparisons between the checks of precipitated $CaCO_3$ and the untreated soil, however, permitted no such assumption.

A summation of the analyses from the twelve cylinders, to which the 2-ton treatments were applied, points conclusively to one fact, namely, that not all of the oxide and hydrate treatments were absorbed as such, prior to carbonation. Furthermore, the oxide and hydrate treatments reached their maximum carbonation within 5 days and then followed absorption of lime from the carbonate. During the succeeding 5 days there was effectuated maximum immediate absorption from the lighter treatment. This is borne out by the following data. The average of 24 determinations upon the twelve cylinders which received the same amount of CaO as burnt oxide or hydrate gave 0.0450 per cent CO_2 at the end of 61 days of contact between soil and treatment; while the average of 8 determinations upon the precipitated $CaCO_3$ checks gave 0.0437 per cent CO_2. But, the average of 24 determinations from the twelve cylinders at the end of 5 days of contact between lime and soil gave an occurrence of 0.0830 per cent CO_2. During the succeeding 5 days, however, there occurred a decrease in the CO_2 content of these twelve cylinders to 0.0449 per cent, as an average from 24 determinations. Thus for 5, 10 and 61 days of contact, the CO_2 occurrences indicated by the analyses were 0.0830 per cent, 0.0449 per cent and 0.0450 per cent, respectively, from a treatment of 2 tons per acre of CaO, as compared to 0.0437 per cent for the final residual CO_2 content from the equivalent treatments of precipitated $CaCO_3$.

Eight-ton treatments. The 8-ton treatments in the cylinders furnished considerable excess of lime above the immediate absorption coefficient. They thus afforded better opportunity for chemical analysis and a more satisfactory basis of comparison than was possible in the case of the 2-ton treatments. The analyses of the 8-ton treatments are given in tables 17 to 21, inclusive. As a whole, the soils of the 8-ton treatments may be said to have effected complete carbonation during the period extending between 19 and 38 days after treatment. No difference could be noted between the rate of carbonation in moist soil, without supplementary rainfall and the soil which received water, except possibly during the first period of 15 days. Nor could there be observed any difference between the activities of the oxide and hydrate forms. In comparing the treatments of burnt and hydrated lime when applied alone, and when supplemented by dry barnyard manure no acceleration of carbonate formation could be attributed to the action of the barnyard manure. As differing from the cylinders receiving the lighter applications, it is quite possible that partial retardation of biological activities may have resulted from the 8-ton treatments. This would influence CO_2 evolutions, both in regard to that derived from decomposition of initial organic matter and that derived from the supplementary treatments of barnyard manure. Hutchinson (37) demonstrated a distinct sterilizing effect from treatments of CaO above 0.5 per cent. However, the soils used by

TABLE 21

Comparison between total amounts of $CaCO_3$ *residual from chemically equivalent amounts of* CaO, $Ca(OH)_2$ *and "c.p." precipitated* $CaCO_3$ *when in excess of lime requirements, after contact between treatment and moist acid Cumberland loam soil in field-cylinders*

Basis of treatment 8 tons CaO *per 2,000,000 pounds of soil*

LABORATORY NUMBER	CYLINDER NUMBER	TIME OF CONTACT	TREATMENT	MOISTURE AT TIME OF SAMPLING	CO_2 MOIST SOIL	CO_2 MOISTURE-FREE SOIL	$CaCO_3$ MOISTURE-FREE SOIL	AVERAGE $CaCO_3$ MOISTURE-FREE SOIL		AVERAGE RESIDUAL OF $CaCO_3$ FROM CaO AND $Ca(OH)_2$, AS COMPARED WITH THAT RESIDUAL FROM $CaCO_3$ EQUIVALENT TREATMENT
		days		*per cent*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*
2674	L25	47	CaO, no H_2O applied	11.58	0.3812	0.4310	0.980			
2675	L26	47	$Ca(OH)_2$, no H_2O applied	8.47	0.3900	0.4261	0.970			
2671	L19	47	CaO and 48T. manure, no H_2O	12.67	0.3952	0.4525	1.028	Eight oxide and hydrate cylinders	1.027	96.1
2672	L20	47	$Ca(OH)_2$, 48 T. manure, no H_2O	11.56	0.4074	0.4607	1.047			
2676	L27	47	$CaCO_3$, no H_2O applied	12.81	0.4212	0.4831	1.098			
2689	M25	47	CaO, water applied	15.53	0.3722	0.4404	1.001			
2690	M26	47	$Ca(OH)_2$ water applied	15.54	0.3858	0.4568	1.038			
2686	M19	47	CaO and 48 T. manure, and H_2O	16.03	0.3982	0.4741	1.077	Two checks	1.069	
2687	M20	47	$Ca(OH)_2$ and 48 T. manure, and H_2O	14.13	0.4058	0.4726	1.074			
2691	M27	47	$CaCO_3$, water applied	15.40	0.3871	0.4576	1.040	Difference	0.042	

2704	L25	61	CaO, no H_2O applied	10.38	0.3922	0.4376	0.994			
2705	L26	61	$Ca(OH)_2$, no H_2O applied	12.23	0.3844	0.4377	0.994	Eight oxide and hydrate cylinders	1.024	96.6
2701	L19	61	CaO and 48 T. manure, no H_2O	10.69	0.4076	0.4564	1.037			
2702	L20	61	$Ca(OH)_2$, and 48 T. manure, no H_2O	12.00	0.4002	0.4547	1.033			
2706	L27	61	$CaCO_3$, no water applied	12.06	0.4012	0.4562	1.037			
2720	M25	61	CaO, water applied	16.63	0.3892	0.4612	1.048			
2721	M26	61	$Ca(OH)_2$, water applied	15.72	0.3722	0.4415	1.003			
2717	M19	61	CaO, 48 T. manure, and H_2O	15.98	0.3730	0.4440	1.009	Two checks	1.060	
2708	M20	61	$Ca(OH)_2$, 48 T. manure, and H_2O	16.18	0.3944	0.4706	1.070			
2722	M27	61	$CaCO_3$, water applied	15.97	0.4006	0.4768	1.083	Difference	0.036	

Hutchinson were initially calcareous and hence absorbed little if any of the hydrate; while the cylinder soil was distinctly acid before treatment, and consequently the process of absorption quickly removed a considerable part of the applied lime from the active hydrate form.

Considering the possibility of errors involved in sampling and analysis, it may be said that the occurrence of carbonates was constant after 38 days of contact between lime and soil. The analyses of check treatments of precipitated $CaCO_3$ at the end of 47 and 61 days showed that the check treatments had also reached a state of apparent equilibrium.

In table 21 are given the percentages of carbonate produced by the carbonation of caustic lime and the amount of residual carbonates from the check treatments of precipitated $CaCO_3$, at the end of the longest two intervals between placing and sampling. The average of the eight oxide and hydrate treatments are 0.042 and 0.036 per cent less than the average of the two $CaCO_3$ applications for the 47- and 61-day periods, respectively. The variations between the two checks at each interval are greater than the differences above given as occurring between the soils receiving the two forms of lime. If instead of two checks, eight checks were available to average against 8 cylinders receiving oxide and hydrate treatments, the slight discrepancy might be eliminated. It might be argued, however, that the difference is real. It could be held that the active mass of dissociated calcium ions was greater in the hydrate than in the carbonate and that considerable part of the more strongly dissociated hydrate was in contact with the soil for a number of days prior to carbonation. This would quite probably result in greater absorption of calcium from the hydrate treatment than from a chemically equivalent amount of the less soluble $CaCO_3$. Again, it might be maintained that where no water was added small lumps of lime were carbonated only on the surface of the lumps, and that this carbonate layer would protect enclosed portions of uncarbonated hydrate. However, in view of the thorough dissemination effected and the extreme fineness of the lime and also the chance for absorption of carbonated soil water, such a contention would seem altogether untenable. Furthermore, it might be contended that a part of the lime acted upon or combined with organic matter in such a way as to decrease the amount of lime available for direct carbonation. However, if it be granted that the assumed chemical action of lime upon organic matter is such as to cause a generation of CO_2, the above contention would be invalidated; for it will be shown, by the data of tables 54 and 55, that no such gaseous generation is brought about.

Again, it might be held that the flocculation produced by the uncarbonated lime would result in a physical occlusion of part of the lime that would result in the removal of the lime so occluded from the sphere of chemical activity. Such a viewpoint could not well be disproved. As a matter of fact, it will be shown in the lysimeter studies that after treatment with burnt lime we are unable to obtain at any period, amounts of $CaCO_3$ equivalent to the car-

bonate residual from chemically equivalent amounts of the precipitated carbonate used as a check. And, since the difference between the amounts of lime leached from the two forms and the differences in amounts used in neutralizing acids engendered by nitrification and sulfofication would not account for the deficiency of the carbonate resulting from applications of burnt lime, it is necessary to assume such a physical occlusion or else a greater absorption of lime from the solution phase of $Ca(OH)_2$. The latter would seem to be more in consonance with the chemistry of the problem.

TABLE 22

Showing periodical variations of carbonate-blank CO_2, either actually occurring in cylinder blanks receiving manure alone, or errors introduced in sampling and analysis

NUMBER OF DAYS BETWEEN TREATMENT AND SAMPLING	SOIL APPLICATIONS OF DRY BARNYARD MANURE, AT RATES PER 2,000,000 POUNDS OF MOISTURE-FREE SOIL					
	24,000 lbs.		60,000 lbs.		96,000 lbs.	
	CO_2 in moisture-free soil		CO_2 in moisture-free soil		CO_2 in moisture-free soil	
	No water applied	Water applied	No water applied	Water applied	No water applied	Water applied
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
5	0.0334	0.0061	0.0355	0.0563	0.0107	
10	0.0336	0.0160	0.0170	0.0039	0.0187	0.0135
19	0.0044	0.0211	0.0041	0.0020	0.0075	0.0038
38	0.0134	0.0171	0.0258	0.0293	0.0264	0.0286
47	0.0243	0.0290	0.0316	0.0261	0.0313	0.0276
61	0.0290	0.0333	0.0316	0.0309	0.0318	0.0325
Variations, minimum to maximum.....	0.0298	0.0272	0.0314	0.0543	0.0233	0.0287

Consideration of analytical error involved in the determination of carbonates in the cylinders

By reference to table 22, the reader will see the differences which may be expected in the determination of the meagre amounts of CO_2 in that series of checks which have been treated with manure without lime. The deviations and fluctuations may be considered as real, or as being due to error introduced through sampling or through chemical manipulation. In only one instance is the variation between maximum and minimum of the magnitude of the difference found between the CaO and $Ca(OH)_2$ treatments and the $CaCO_3$ checks. Hence, it might be assumed, within reason, that a part of the determined deficiency of $CaCO_3$ below that of theory resulting from the CaO and $Ca(OH)_2$ treatments may be actually attributable to the several possible limiting factors discussed in the preceding paragraph. The amounts of $CaCO_3$ derived from the residual CaO and $Ca(OH)_2$, not absorbed directly by the soil are consistently, though not materially, less than those remaining

from the equivalent applications of $CaCO_3$. However, without supplementary data, the differences are not of such magnitude as to justify the unqualified statement that the two caustic forms have been more active than the precipitated carbonate in the neutralization of acid soils. But, when fortified by the residual carbonate and leaching data obtained later in the 8-ton CaO lysimeter treatments, it would seem conservative to conclude that more lime has been absorbed by the soil from the oxide and hydrate mixed throughout the soil, than from equivalent amounts of precipitated $CaCO_3$ incorporated in the soil simultaneously and in the same manner. Again, further data obtained in other analyses of the same series of cylinders demonstrated the fact that more lime was absorbed by the soil from treatments of precipitated $CaCO_3$ than from equivalent and simultaneous treatments of ground limestone. Since the precipitated $CaCO_3$ was more soluble than the limestone, this would be expected and it is in accord with the differences manifested between the oxide, or hydrate, and precipitated carbonate. It would appear then, that in a given time the extent of absorption, fixation or silication by the soil of equivalent and simultaneous applications of calcareous materials would vary with the material applied. Burnt and hydrated lime seem identical and are first in order followed by precipitated carbonate, and it in turn by limestone.

POT STUDIES IN THE FIELD

In the foregoing field cylinder studies, the carbonation problem represented but one phase of the problem as a whole. In the more comprehensive problem which embraced the carbonation studies it was necessary that all of the treatments applied should be worked thoroughly throughout the entire volume of soil, in order to justify the sampling which was planned for the other subsequent work that was to extend over a long period. Hence, in the cylinder carbonation studies, the mixing of lime with the acid soil involved a conflict of the carbonation and absorption factors which has been discussed in preceding paragraphs. The lightest cylinder treatment mixed with soil was based upon a 4000-pound application for each 2,000,000 pounds of moisture-free soil. It seemed desirable, therefore, to attempt a study of the carbonation of a treatment equivalent to the more common application of 2000 pounds per acre surface. The cylinder experiments with but one loam soil, previously discussed, demonstrate that such an application would have been so speedily absorbed by the acid soil as to make impossible a reliable quantitative study of the formation of $CaCO_3$. It was necessary, therefore, to eliminate or minimize this factor of absorption. This was done by subjecting seven acid soils to a preliminary treatment with precipitated $CaCO_3$. Such a preliminary treatment would so vitiate the normal condition of the acid soil as to make it imperative that time be allowed for a return to normality before application of $Ca(OH)_2$. In addition, it appeared advisable

to consider the possible influence of the reaction of the soil immediately underlying that with which the lime was to be mixed; this, because of the possible differential introduced by variation of soil reaction in influencing the extent of upward diffusion of CO_2 from the underlying soil to that overlying and mixed with $Ca(OH)_2$; as well as the contention that so-called acids other than H_2CO_3 will diffuse, upward from an acid soil. Accordingly ten pots were filled with each of seven soils. Each pot was given its respective preliminary and experimental treatment as outlined in table 23. Thirty-five of the pots were used to contain seven checks and 28 treatments which were to be sampled at the end of 4 days, and the same number were to be used for a second sampling, which was to be made at a time indicated as desirable by

TABLE 23

Weights of soils in pots (total and by zones); amounts of $CaCO_3$ *used in preliminary treatments and amounts of* $Ca(OH)_2$ *applied*

SOILS USED	WET SOIL PER ENTIRE POT	WET SOIL PER UPPER ZONE	WET SOIL PER LOWER ZONE	MOISTURE-FREE SOIL PER ENTIRE POT	MOISTURE-FREE SOIL PER UPPER ZONE	MOISTURE-FREE SOIL PER LOWER ZONE	$CaCO_3$ PER ENTIRE POT	$CaCO_3$ PER UPPER ZONE	$CaCO_3$ PER LOWER ZONE	$Ca(OH)_2$ SURFACE AND MIXED THROUGHOUT UPPER ZONE $\Leftrightarrow$ 2000 POUNDS CaO PER 2,000,000 POUNDS OF SOIL
	gm.	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
Jackson sandy loam	2214	1377	837	2162	1345	817	10.8010	6.7175	4.0835	1.7950
Cherokee sandy loam	2066	1350	716	1914	1251	663	9.5695	6.2545	3.3150	1.6701
Dolomitic gravelly loam	2417	1345	1072	2226	1239	987	11.1315	6.1945	4.9370	1.6541
Indian mound loam	2324	1377	947	2093	1240	853	10.4630	6.1995	4.2635	1.6554
Second bench loam	2276	1389	887	1997	1219	778	9.9840	6.0930	3.8910	1.6269
Chickamauga loam	2389	1425	964	2005	1196	809	10.0245	5.9795	4.0450	1.5967
Tellico sandy loam	2044	1184	860	1783	1033	750	8.9150	5.1640	3.7510	1.3789

$CaCO_3$ treatments based upon treatment of 10,000 pounds of carbonate per 2,000,000 pounds of moisture-free soil.

the results secured from the first sampling. The details of the experiment were as follows: The clay pots used were 8 inches in depth and 7 inches in diameter. They were painted on the outside with black asphaltum paint, except on the bottom, which were left unpainted. The outlets for drainage were unstoppered. Immediately after the preliminary $CaCO_3$ treatment, the pots were imbedded in the soil outdoors, where they were left exposed for a period of 14 months. The $CaCO_3$ treatments were made at the rate of 10,000 pounds of $CaCO_3$ per 2,000,000 pounds of moisture-free soil. In one-half of the number of pots used the entire 6 inches of soil was treated with $CaCO_3$ at this rate. In the remaining pots, the upper 3-inch zone received the preliminary $CaCO_3$ treatment, but the lower zone was unaltered,

TABLE 24

Comparison between the reversion of hydrated lime to carbonate, when exposed on the surface and when mixed within the upper 3 inches of soils; embedded pot containers; treatments equivalent to CaO *at the rate of 2,000 pounds per 2,000,000 pounds of soil*

SOIL	WHERE ENTIRE 6 INCHES OF SOIL WERE GIVEN AN APPLICATION OF $CaCO_3$ AT THE RATE OF 10,000 POUNDS PER 2,000,000 POUNDS OF SOIL 14 MONTHS PRIOR TO APPLICATION OF $Ca(OH)_2$									WHERE UPPER 3 INCHES ONLY WERE TREATED WITH $CaCO_3$ AT THE RATE OF 10,000 POUNDS PER 2,000,000 POUNDS OF SOIL 14 MONTHS PRIOR TO APPLICATION OF $Ca(OH)_2$								
	Blank	Increase in CO_2 content of soils over blanks after applications of $Ca(OH)_2$								Blank	Increase in CO_2 content of soils over blanks after applications of $Ca(OH)_2$							
		Applied to surface				Mixed with 3 inches of soil					Applied to surface				Mixed with 3 inches of soil			
		After 4 days		After 10 days		After 4 days		After 10 days			After 4 days		After 10 days		After 4 days		After 10 days	
		As CO_2 in soil	As per cent carbonation	As CO_2 in soil	As per cent carbonation	As CO_2 in soil	As per cent carbonation	As CO_2 in soil	As per cent carbonation		As CO_2 in soil	As per cent carbonation	As CO_2 in soil	As per cent carbonation	As CO_2 in soil	As per cent carbonation	As CO_2 in soil	As per cent carbonation
	gm.	*gm.*	*per cent*	*gm.*	*per cent*	*gm.*	*per cent*	*gm.*	*per cent*	*gm.*	*gm.*	*per cent*	*gm.*	*per cent*	*gm.*	*per cent*	*gm.*	*per cent*
Jackson sandy loam	0.048	0.091	115	0.072	91	0.068	86	0.066	84	0.045	0.056	71	0.070	89	0.056	71	0.070	89
Cherokee sandy loam	0.015	0.080	101	0.019	25	0.033	42	0.042	53	0.014	0.050	63	0.050	63	0.036	46	0.042	53
Dolomitic gravelly loam	0.155	0.110	139	0.078	99	0.096	122	0.085	108	0.173	0.092	116	0.036	46	0.041	52	0.049	62
Indian mound loam	0.020	0.086	109	0.058	73	0.037	47	0.036	46	0.011	0.085	108	0.049	62	0.042	53	0.047	60
Second river bench loam	0.046	0.064	81	0.074	94	0.059	75	0.058	73	0.031	0.083	105	0.077	97	0.066	84	0.059	75
Chicamauga loam	0.101	0.086	109	0.073	92	0.073	92	0.069	87	0.093	0.118	149	0.084	106	0.065	82	0.065	82
Tellico sandy loam	0.011	0.042	53	0.030	38	0.021	27	0.029	37	0.011	0.037	47	0.044	56	0.029	37	0.024	30
Averages	0.057	0.080	108	0.058	75	0.055	70	0.055	70	0.056	0.074	94	0.059	74	0.048	61	0.051	64

save for sifting and mixing. Each upper and lower 3-inch zone was separated by a galvanized iron wire disc made from $\frac{1}{8}$-inch wire cloth. To each disc was attached galvanized wire handles, which permitted the removal of the upper zone *en bloc*, without disturbing the lower zone. At the end of the 14 months' exposure, the lime treatments were applied. Hydrated lime, 99.86 per cent pure, was mixed through the entire upper 3-inch zone of one-half the number of pots, while the remaining pots received the lime on the soil surfaces. The upper zones of the check pots were removed, mixed and replaced in the same manner as were those of the pots receiving $Ca(OH)_2$. The 14 months' exposure would seem to represent a reasonable period, during which the $CaCO_3$-treated soils would be expected to return to a nearly normal condition; however, such a period also afforded an opportunity for the relatively soluble precipitated carbonate to leach out and leave the soil with a further tendency to absorb additional quantities of lime. Four days after the application of hydrated lime one-half of the total number of pots was conveyed to the laboratory and dried in electric ovens at 105°C. The remaining pots were sampled and analyzed at the end of 10 days of exposure. The data secured in this manner are incorporated in table 24. The relative meagreness of the amount of hydrate applied and the difficulties of technic are responsible for limitations which may well be considered.

Discussion of the data of table 24

The data of this table serve as a good illustration of the difficulty encountered in recording chemical changes resulting from soil treatments in amounts which would be considered as within the limits of good practice. An increase of 0.079 per cent represents the theoretical increase of CO_2 which would be possible from the lime applied at the 1-ton rate. A relatively small percentage of error, therefore, represents a considerable proportion of the total of the amount representing the possible increase.

In addition, certain insuperable but essential conditions of control tended to vitiate the results. In working with so many samples at the same time it was necessary to heat simultaneously, immediately after their removal from the pots in the field, in order to eliminate moisture and inhibit any further generation of CO_2. This would be expected to augment the amount of lime absorbed by the soil in the case of the mixtures of lime throughout the soil, while it would cause but slight, if any, absorption in the case of the surface treatments, which were in contact with but a fraction of the whole amount of soil.

Again, the simultaneous heating of the contents of each of the 35 pots, of each period of exposure, in two large electric ovens, occasioned the giving-off of the CO_2 content of the soil moisture, and possibly some of that condensed upon surfaces of the soil particles. Any residual hydrate of that internally or externally applied would thus have access to moist atmospheric CO_2.

Considering the averages obtained from the seven soils, it appears that there was no enhancement in the gain of $CaCO_3$ at the end of 10 days, as compared to that found at the end of 4 days; this applying to both surface and intra-soil treatments. Nor does it appear that any difference was registered between the soil underlaid with 3 inches of acid soil as compared to that which was underlaid with 3 inches of alkaline soil. Furthermore, recognizing the limitations above referred to, it would seem that one of two conclusions is possible. Either all of the lime mixed within and applied to the surface at the rate of 1 ton per 2,000,000 pounds of soil, had reverted to the carbonate at the end of 4 days, or any residual hydrate occurring at the time of sampling was converted to the carbonate by the CO_2 given off in the ovens during the process of drying. It is possible, however, that the CO_2 derived from field exposure and from oven-drying brought about the maximum carbonation to be effected with lime of the fineness of that exposed: but, had there been induced a disruption of the pseudo-equilibrium through wetting or grinding, there might have occurred a greater average in the gain of carbonate CO_2.

It is evident from the foregoing that in order to secure data of positive nature and value it is essential that a heavier rate of application, fewer soils, and smaller amounts be employed, under conditions permitting better contact and speedier manipulation.

Accordingly, further experiments were planned, which are reported under the designation of "Tumbler experiments."

CARBONATION STUDIES IN FIELD LYSIMETER TANKS

The study of the carbonation resulting from exposure of burnt and hydrated lime in the originally acid Cumberland loam soil of the cylinders was continued by the installation, in July, 1914, of a lysimeter field equipment. This permits of determination of both residual transformations and natural leachings.

The lysimeter tanks are illustrated in plate 2, figures 1 and 2. The tanks are placed in a single row along the top of the terrace, against which is built a supporting re-enforced concrete wall 7 feet high. This wall is paralleled by an outer concrete block wall of same length and height. At the upper end broad steps lead from the terrace above down to the concrete walk which runs parallel to and between the retaining and outer walls. The concrete walk has a trough running its entire length to care for the discarded surplus of leachings. At the other end a retaining wall extends the width of the walk at right angles thereto, connecting the two long walls. The enclosure is lighted by 7 windows placed in the long outer wall, by 6 panes of glass 26 by 32 inches in the roof, and by 2 sash doors, one in the upper end and the other in the long outer wall at its lower end. Electric wiring is also installed. The structure has a tight asphaltum-covered wooden roof. The leachings

from the treated soils are caught and stored in galvanized iron cans. These are painted with black asphaltum paint, and this in turn is coated with paraffin. Close-fitting tops prevent intrusion of light and evaporation of the leachings during their accumulation. The leachings are drained from the sand filters at the base of the tanks to the cans by means of block-tin tubes. As rainfall and leaching demand, the leachings are conveyed to the laboratory where their alkalinity and nitrate content are determined. Aliquots also are taken for acidified composite samples. These composites are then analyzed annually, or as often as may seem advisable.

That part of the installation devoted to the study of the activities of the several forms of lime embraces a total of 46 tanks, each tank being of 1/20,000 acre in area. Only 12 of the tanks are devoted to the present carbonation studies. One series contains surface soil only. This series, comprising 23 tanks, rests on a filter formed by 1 inch of clean sand. A second series of 23 tanks contain surface soil, underlaid by 12 inches of red clay subsoil, which in turn rests on the sand filters. The surface soil in each tank was about 8 inches deep when in loose tilth, and amounted to 100 pounds of moisture-free soil. As in the cylinder experiments, sufficient moist acid soil was dug nearby, screened through a $\frac{1}{4}$-inch mesh sieve and thoroughly mixed. While being carted to the lysimeter tanks, and also during the overnight period required for moisture determinations and calculations to a moisture-free basis, the soil was kept closely covered. The soil used in the tanks was taken from the same river bench from which the cylinder soil was obtained. It was, however, somewhat less cherty and more loamy than the soil of the cylinders.

In this experiment pulverized, freshly burnt lime was used against precipitated chalk as a check. In the cylinder experiments no appreciable difference was noted between the carbonation of the water-slaked lime applied and that of the burnt lime applied to and slaked in the moist soil. The parallel between CaO and $Ca(OH)_2$ was therefore not continued in the lysimeter experiments. Treatments were based upon applications of 8, 32 and 100 tons of CaO per 2,000,000 pounds of moisture-free soil. Analysis of the burnt lime gave an equivalence of approximately 93 per cent CaO and a trace of both MgO and CO_2. It is, of course, not to be contended that results obtained from the two larger treatments are capable of practical application. The use of the large amounts is, however, justified by academic and scientific requirements. With treatments of less than 8 tons, small and almost invariably plus analytical errors assume proportions relatively large in percentage, as compared with treatments given. But with the larger treatments and greater differences, we are more fully justified in drawing conclusions from analytical results. However, in the case of the heavier treatments greater homogeneity of the treated soil is essential and most likely the probability of error in the sampling of the smaller charges is coincidentally enhanced. Furthermore, the heavy treatments bring about conditions

markedly different from those resulting from the light applications. This is particularly true with reference to volume and differences of physical and biological nature.

As in the case of the cylinders, chemical equivalence was determined by titration and the treatments were sealed and conveyed to the field equipment in large bottles. In this experiment the entire 8 inches of moist soil and treatment were mixed in metal-lined boxes before placing in the lysimeters. At periods of 10, 17, 32, 49, 74, 218 days and at the end of 1, 2, 3 and 4 years subsequent to placing, samples were collected from the tanks which received

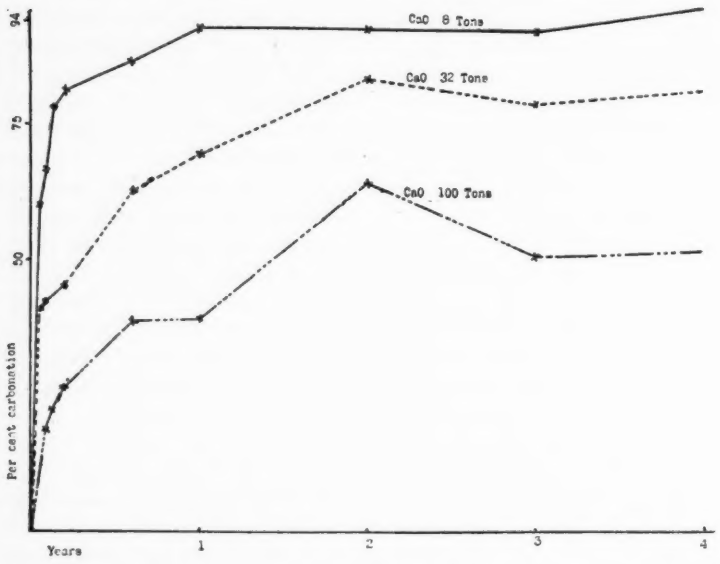

FIG. 3. SPEED OF THE REVERSION OF CaO TO $CaCO_3$, WHEN APPLIED TO THE CUMBERLAND LOAM IN THE LYSIMETERS, DISREGARDING THE LOSS BY LEACHING AND THE VARIATIONS IN WEIGHT OF THE APPLICATIONS (TABLES 25 TO 30)

oxide and carbonate check treatments. Borings were made with butter samplers to the full depth of the surface soil. The small samples thus secured were quickly dried by exposure in thin layers to the direct rays of the sun. They were then passed through a 0.5mm. sieve and analyzed for $CaCO_3$. At the end of 1, 2, 3 and 4-year periods, samples of the upper and lower halves of the entire depth were collected in order to study surface and subsurface carbonation. In the case of the heaviest applications, the applied materials resulted in a depth greater than the original 8 inches. The averages of duplicate determinations made upon the annual samplings from the upper and lower zones were used to obtain the average composition of the whole

depth. The residual carbonates resulting from applied CaO are compared periodically with the residual $CaCO_3$ of the precipitated carbonate checks in tables 25 to 30, inclusive. In these tables, the loss by leaching is not taken into consideration. It was, of course, almost impossible to correlate the

TABLE 25

Carbonation of freshly burnt pulverized unslacked lime when mixed with moist acid Cumberland loam soil without subsoil in field lysimeter tanks, during a period of 4 years as derived from determinations of residual carbonates, disregarding differential leachings; rate of applications 8 tons of 93 per cent CaO *per acre 2,000,000 pounds of moisture-free soil*

LABORATORY NUMBER	TANK NUMBER	PERIOD BETWEEN TREATMENT AND SAMPLING	CO_2 IN MOISTURE-FREE SOIL	$CaCO_3$		CARBONATION AS COMPARED WITH $CaCO_3$ CHECK
				In moisture-free soil	Per acre 2,000,000 pounds of moisture-free soil	
			per cent	*per cent*	*lbs.*	*per cent*
3344	1	10 days				
3346	3	10 days				
3388	1	17 days	0.2151	0.4888	9,776	54.6
3390	3	17 days	0.3958	0.8955	17,910	
3430	1	32 days	0.2536	0.5763	11,526	63.2
3432	3	32 days	0.4001	0.9115	18,230	
3506	1	49 days	0.2929	0.6657	13,314	79.7
3508	3	49 days	0.3674	0.8350	16,700	
3631	1	74 days	0.3191	0.7252	14,504	77.6
3633	3	74 days	0.4111	0.9343	18,686	
4120	1	218 days	0.3314	0.7532	15,064	84.8
4122	3	218 days	0.3906	0.8877	17,754	
4162	1	1 year	0.3425	0.7783	15,568	92.8
4166	3	1 year	0.3691	0.8388	16,776	
4596	1	2 years	0.3068	0.6974	13,948	92.9
4598	3	2 years	0.3304	0.7508	15,016	
4894	1	3 years	0.282	0.641	12,820	93.2
4898	3	3 years	0.303	0.688	13,760	
5389	1	4 years	0.131	0.303	6,060	89.6
5393	3	4 years	0.149	0.338	6,760	

fractional leachings of the initial annual period with periodic determinations of residual carbonates during the relatively short periods. However, at the end of each annual period, complete analyses were made of the composite of leachings for the preceding year. These analyses afford the data of table 31.

Carbonation effected in the 8, 32 and 100-ton treatments of the lysimeter tanks

The treatments of CaO in the leaching tanks range from a minimum of 8 tons to a maximum of 100 tons per 2,000,000 pounds of soil. The effects

TABLE 26

Carbonation of freshly burnt, pulverized, unslacked lime when mixed with moist acid Cumberland loam soil overlying 12 inches of acid red clay subsoil in field lysimeter tanks, during a period of 4 years as derived from determinations of residual carbonate, disregarding differential leachings; rate of application 8 tons of 93 per cent CaO *per acre 2,000,000 pounds of moisture-free soil*

LABORATORY NUMBER	TANK NUMBER	PERIOD BETWEEN TREATMENT AND SAMPLING	CO_2 IN MOISTURE-FREE SOIL	$CaCO_3$		CARBONATION AS COMPARED WITH $CaCO_3$ CHECK
				In moisture-free soil	Per acre 2,000,000 pounds of moisture-free soil	
			per cent	*per cent*	*lbs.*	*per cent*
3365	22	10 days	0.2417	0.5493	10,986	62.1
3367	24	10 days	0.3895	0.8852	17,704	
3409	22	17 days	0.2557	0.5811	11,622	65.1
3411	24	17 days	0.3929	0.8929	17,858	
3442	22	32 days	0.2691	0.6116	12,232	68.7
3444	24	32 days	0.3945	0.8966	17,932	
3518	22	49 days	0.2897	0.6584	13,168	74.9
3520	24	49 days	0.3863	0.8779	17,558	
3643	22	74 days	0.3535	0.8034	16,068	83.7
3645	24	74 days	0.4223	0.9597	19,194	
4132	22	218 days	0.3523	0.8007	16,014	86.4
4134	24	218 days	0.3830	0.8704	17,408	
4186	22	1 year	0.3339	0.7588	15,176	90.9
4190	24	1 year	0.3670	0.8341	16,682	
4620	22	2 years	0.2969	0.6804	13,608	91.1
4622	24	2 years	0.3279	0.7471	14,942	
4918	22	3 years	0.266	0.604	12,080	88.4
4922	24	3 years	0.300	0.683	13,660	
5413	22	4 years	0.283	0.643	12,860	101.1
5417	24	4 years	0.280	0.636	12,720	

produced are very striking. The heavier treatments produce conditions which are not common to the lighter treatments.

The 8-ton treatments will be first considered. The data obtained from the tanks receiving applications at this rate are recorded in tables 25 and 26.

During the first 10 days after treatment the production of carbonate amounted to over 68 per cent of that indicated by the check as being complete recarbonation. The speed of $CaCO_3$ formation in the tanks was decidedly less rapid than that observed where the same amount of lime was applied to the

TABLE 27

Carbonation of freshly burnt, pulverized, unslacked lime when mixed with moist acid Cumberland loam soil without subsoil in field lysimeter tanks, during a period of 4 years as derived from determinations of residual carbonates, disregarding differential leachings; rate of application 32 tons of 93 per cent CaO *per acre 2,000,000 pounds of moisture-free soil*

LABORATORY NUMBER	TANK NUMBER	PERIOD BETWEEN TREATMENT AND SAMPLING	CO_2 IN MOISTURE-FREE SOIL	$CaCO_3$		CARBONATION AS COMPARED WITH $CaCO_3$ CHECK
				In moisture-free soil	Per acre 2,000,000 pounds of moisture-free soil	
			per cent	*per cent*	*lbs.*	*per cent*
3351	8	10 days				
3353	10	10 days				
3395	8	17 days	0.8128	1.847	36,940	38.4
3397	10	17 days	2.112	4.800	96,000	
3434	8	32 days	0.8259	1.877	37,540	38.7
3436	10	32 days	2.132	4.845	96,900	
3510	8	49 days	0.8119	1.843	36,860	38.8
3512	10	49 days	2.084	4.743	94,860	
3635	8	74 days	0.9851	2.2389	44,778	44.0
3637	10	74 days	2.2396	5.0886	101,772	
4124	8	218 days	1.2917	2.9357	58,714	61.1
4126	10	218 days	2.1137	4.8039	96,078	
4170	8	1 year	1.5201	3.4548	69,096	72.1
4174	10	1 year	2.1098	4.7950	95,900	
4606	8	2 years	1.6396	3.7264	74,528	80.8
4608	10	2 years	2.0285	4.6101	92,202	
4902	8	3 years	1.462	3.322	66,440	73.6
4906	10	3 years	1.987	4.516	90,320	
5397	8	4 years	1.465	3.329	66,580	72.4
5401	10	4 years	2.032	4.598	91,960	

cylinders in the same month of the preceding year. There was, however, a decided difference in the tilth maintained in the two experiments. As previously noted, only light showers fell upon the cylinder soils prior to complete carbonation of applied lime. As a result, the cylinder soils were of granular

structure during the period between application and the attainment of maximum carbonation. But the tank soils were saturated by heavy rains shortly after they were placed in the tanks and from the beginning they were, there-

TABLE 28

Carbonation of freshly burnt pulverized, unslacked lime when mixed with moist acid Cumberland loam soil overlying 12 inches of red clay acid subsoil in field lysimeter tanks, during a period of 4 years, as derived from determinations of residual carbonates, disregarding differential leachings; rate of application 32 tons 93 per cent CaO *per acre 2,000,000 pounds of moisture-free soil*

LABORATORY NUMBER	TANK NUMBER	PERIOD BETWEEN TREATMENT AND SAMPLING	CO_2 IN MOISTURE-FREE SOIL	$CaCO_3$		CARBONATION AS COMPARED WITH $CaCO_3$ CHECK
				In moisture-free soil	Per acre 2,000,000 pounds of moisture-free soil	
			per cent	*per cent*	*lbs.*	*per cent*
3372	29	10 days				
3374	31	10 days				
3416	29	17 days	0.8673	1.971	39,420	43.2
3418	31	17 days	2.005	4.557	91,140	
3446	29	32 days	0.9378	2.131	42,620	45.2
3448	31	32 days	2.073	4.711	94,220	
3522	29	49 days				
3524	31	49 days				
3647	29	74 days	0.9818	2.2927	45,854	47.3
3649	31	74 days	2.1332	4.8482	96,964	
4136	29	218 days	1.3348	3.0336	60,672	63.3
4138	31	218 days	2.1410	4.8659	97,318	
4194	29	1 year	1.3760	3.1272	62,544	66.6
4198	31	1 year	2.0616	4.6859	93,718	
4628	29	2 years	1.729	3.9269	78,538	83.7
4632	31	2 years	2.0652	4.6936	93,872	
4926	29	3 years	1.598	3.631	72,620	80.9
4940	31	3 years	1.975	4.489	89,780	
5421	29	4 years	1.740	3.953	79,060	86.8
5425	31	4 years	2.005	4.556	91,120	

fore, in a much more compact condition. This difference in tilth and variation in pore space evidently had a marked influence upon oxidation and diffusion of soil atmosphere. Using the residual carbonates as the basis of comparison, only 92 per cent and 91 per cent carbonation was effected in

tanks 1 and 22, respectively, at the end of one year. If at the end of the first year, we add to the residual carbonate found in the oxide tank 1, the $CaCO_3$ equivalence of the excess of its total lime leached above that of its carbonate-check tank, a percentage carbonation of 95 is obtained. More than twice as

TABLE 29

Carbonation of freshly burnt pulverized unslacked lime when mixed with moist acid Cumberland loam soil without subsoil in field lysimeter tanks during a period of 4 years as derived from determinations of residual carbonates, disregarding differential leachings; rate of application 100 tons of 93 per cent CaO *per acre 2,000,000 pounds of moisture-free soil*

LABORATORY NUMBER	TANK NUMBER	PERIOD BETWEEN TREATMENT AND SAMPLING	CO_2 IN MOISTURE-FREE SOIL	$CaCO_3$		CARBONATION AS COMPARED WITH $CaCO_3$ CHECK
				In moisture-free soil	Per acre 2,000,000 pounds of moisture-free soil	
			per cent	*per cent*	*lbs.*	*per cent*
3358	15	10 days				
3360	17	10 days	6.2978	14.313	286,160	
3402	15	17 days				
3404	17	17 days	6.2631	14.234	284,680	
3438	15	32 days	1.2339	2.804	56,080	19.7
3440	17	32 days	6.2499	14.204	284,080	
3514	15	49 days	1.4232	3.235	64,700	22.5
3516	17	49 days	6.2238	14.145	282,900	
3639	15	74 days	1.6789	3.815	76,300	26.6
3641	17	74 days	6.3160	14.354	287,080	
4128	15	218 days	2.4420	5.550	111,000	39.8
4130	17	218 days	6.1546	13.988	279,760	
4178	15	1 year	2.5059	5.695	113,900	39.8
4182	17	1 year	6.2946	14.305	286,100	
4612	15	2 years	3.9587	8.9971	179,942	63.1
4616	17	2 years	6.2715	14.2534	285,068	
4910	15	3 years	2.767	6.289	125,780	44.7
4914	17	3 years	6.185	14.057	281,140	
5405	15	4 years	3.677	8.357	167,140	60.1
5409	17	4 years	6.122	13.913	278,260	

much $CaCO_3$ was formed during the first month of contact as was formed during the succeeding 11 months. At the close of the succeeding annual periods, practically no further carbonation had ensued. It is difficult to explain the marked decrease in the residual carbonate of the surface soil of

the 8-ton oxide tank and its carbonate check after the third year. Though very marked, the decrease is consistent in the two tanks having no subsoil; but no such corresponding decrease took place in the case of the corresponding

TABLE 30

Carbonation of freshly burnt pulverized unslacked lime when mixed with moist acid Cumberland loam soil, overlying 12 inches of acid red clay subsoil in field lysimeter tanks, during a period of 4 years, as derived from determinations of residual carbonates, disregarding differential leachings; rate of application 100 tons of 93 per cent CaO *per acre 2,000,000 pounds of moisture-free soil*

LABORATORY NUMBER	TANK NUMBER	PERIOD BETWEEN TREATMENT AND SAMPLING	CO_2 IN MOISTURE-FREE SOIL	$CaCO_3$		CARBONATION AS COMPARED WITH $CaCO_3$ CHECK
				In moisture-free soil	Per acre 2,000,000 pounds of moisture-free soil	
			per cent	*per cent*	*lbs.*	*per cent*
3379	36	10 days				
3381	38	10 days	6.1770			
3423	36	17 days	2.2238			
3425	38	17 days	6.1337			
3450	36	32 days	1.0206	2.318	46,360	16.3
3452	38	32 days	5.9906	13.613	272,260	
3526	36	49 days				
3528	38	49 days	6.2523			
3651	36	74 days	1.6231	3.689	73,780	25.6
3653	38	74 days	6.2320	14.391	287,820	
4140	36	218 days	2.2965	5.219	104,380	37.1
4142	38	218 days	6.1964	14.077	281,540	
4202	36	1 year	2.6143	5.941	108,820	38.5
4206	38	1 year	6.2178	14.131	282,620	
4636	36	2 years	4.5476	10.3344	206,688	73.7*
4640	38	2 years	6.1688	14.0199	280,398	
4934	36	3 years	3.014	6.851	137,020	50.2
4938	38	3 years	6.003	13.643	272,860	
5429	36	4 years	2.626	5.968	119,360	43.0
5433	38	4 years	6.102	13.868	277,360	

* Probable error due to second sampling in hole made by previous sampling.

tank which contained subsoil. The year was decidedly subnormal, with reference to rainfall, and the leachings contained less than half as much lime as was contained in either that of the second or third year and only a fourth

of that of the first year. The tanks without subsoil were, as a rule, much drier than the corresponding ones with subsoil during the dry year and it is possible that greater absorption was thereby induced, as a result of a decreased tendency toward the effecting of hydrolysis and reversal of the reaction involved in the absorption of lime by the soil. To the eye, the water-holding capacity of the soils receiving 8-ton treatments appeared to have been materially increased. The treatment did not, however, develop flocculation and granulation to an extent sufficient to offset the tendency of the heavy precipitation to cause saturation, rather than the quick attainment of the optimum condition.

Considering next the data obtained from the 32-ton tanks as given in tables 27 and 28, we find a distinctly greater amount of absolute carbonation, though a considerably less percentage conversion to $CaCO_3$, than was shown by the analysis of the soils receiving 8-ton treatments. The percentage conversion of CaO to $CaCO_3$ increased very slowly after an initial rapid carbonation. During the first 17 days, an average of 40.8 per cent was obtained while a percentage of about 70, was reached at the end of the first year. An additional average increase of about 12 per cent occurred during the second year of contact after which no conclusive evidence of further carbonation was adduced. At the end of 4 years the leachings from the 32-ton tanks, without subsoil, were strongly impregnated with calcium hydroxide. The soils in these tanks underwent a wonderful physical transformation. Drainage from heavy rainfall is now usually complete within a few hours and shortly thereafter the soils attain a very dry state. As will be shown later, marked depression in the evidence of biological activities responsible for CO_2 production also resulted from the heavy treatments applied to these tanks. As a result, the large lime treatment is now contained in a soil often approaching almost air-dry conditions and of a distinct paucity of atmospheric CO_2. Because of this fact, together with the protective action of the dry soil in delimiting infusion of atmosphere, it is not remarkable that only about 80 per cent carbonation has been effected during the 2-year period of exposure.

We come next to consideration of the 100-ton treatments and to discussion of the data of tables 29 and 30. Here we find, though somewhat magnified, the same conditions which characterized the 32-ton applications. After 32 days of contact, more than twice as much actual carbonation is recorded, though a less percentage of conversion has been attained. The increase of carbonate effected during the second, third and fourth years of exposure has been less in percentage, but in extent far greater than that attained in the case of the 32-ton tanks. At the end of the fourth year of exposure, almost 50 per cent of the 100-ton applications is still uncarbonated. As was noted in the case of the 32-ton tanks, the leachings from the 100-ton surface-soil tanks were still strongly impregnated with calcium hydroxide at the end of the fourth year. The same restrictive tendencies noted in the case of the 32-ton tanks also obtain for the 100-ton treatments.

Leaching and other factors involved in comparisons of calcium carbonate residual from equivalent treatments of CaO *and* $CaCO_3$ *in the lysimeter experiments*

In table 31 are given the total amounts of lime leached from the lysimeters during each of the 4 annual periods, beginning July 15, 1914, together with a summary of losses incurred during the entire period of 4 years. These results should be considered in the light of their bearing upon the determination of residual carbonates.

The lysimeter experiments embody comparisons between excessive amounts of CaO in several forms of varying solubilities, over a long period of time, and hence introduce factors which are not involved in the cylinder and other studies. An untreated soil may be compared with one receiving and maintaining 8000 to 32,000 pounds of $CaCO_3$, the latter being the maximum of the cylinder applications and the minimum of the lysimeter treatments, without consideration being given to the weight of the applied material, when interpreting analytical results into terms of pounds per 2,000,000 pounds of soil. Even assuming that the above weights of applied carbonate were not decreased by disintegration through absorption of CaO and liberation of 44 per cent of the respective amounts, applications of 8000 to 32,000 pounds of $CaCO_3$ would amount to but 0.4 per cent and 1.6 per cent, respectively, on the original basis of 2,000,000 pounds of soil, as against 0.3984 per cent and 1.5748 per cent, respectively, on the basis of the augmented weights 2,008,000 and 2,032,000 pounds of soil. These respective differences of 0.0016 per cent and 0.0252 per cent may be considered as well within experimental error incident to sampling and analysis. In using a constant amount of soil and chemically equivalent but different weights of CaO and $CaCO_3$ at the rates of 32 and 100 tons of CaO, there were initially considerable variations in the actual moisture-free weights of the tank contents. These initial differences in moisture-free weights were in part decreased immediately by the hydration of the oxide, which occurred as a result of its access to the soil moisture, and they were still further decreased as the carbonate reaction proceeded. All of the calculations derived from the carbonate analyses were reported in pounds per acre, by the application of analytical results to the original acre, on the 2,000,000-pounds basis. Although close and well within error of sampling and analysis, in the case of the 8-ton treatments, the results are but roughly approximate in the case of the 32 and 100-ton treatments. In the lysimeter experiments there are involved a number of differential and intervening factors, some of which may be determined by chemical analysis, while others must needs be determined by process of elimination. In addition to the problem of variation of weight, the several factors involved may be considered under the following headings.

Absorption and interchange of bases. The absorption of lime may be considered as direct and also as substitutive. In the former case the calcium may be taken up by acid silicates and to some extent by silicic acid, as has

been pointed out by the writer (48), without interchange or liberation of other basic elements. In the latter case, the substitution of calcium for equivalent amounts of the alkali or alkali-earth elements may take place. Such substitution may or may not result in the loss of the liberated bases. It follows that unless enough lime is added to assure an excess of lime after taking care of the tendency of acid silicates to combine directly with lime, there will be little if any liberation of those bases locked up in native silicates. In so far as could be ascertained by examination of leachings, the substitutive activities of the several forms and amounts of lime have been established. These results will later be published. They show relatively little leaching of potassium and sodium. In the cylinder studies, and in the case of the 8-ton treatments in the lysimeters, it was determined that the actual variation in the amounts of direct absorption induced by equivalent amounts of CaO and $Ca(OH)_2$, as compared with $CaCO_3$, was not more than approximately 4 to 5 per cent. It may be, however, that the greater active mass of the solutions resulting from the 32 and 100-ton treatments of CaO has resulted in a more extensive direct absorption of calcium than that which occurred in the respective $CaCO_3$ equivalent checks, but this cannot be definitely established until final equilibrium between $Ca(OH)_2$ and CO_2 shall have been attained.

Sulfofication. In a preliminary report by the writer and associates (51), it was shown that there occurred a wide disparity between the amounts of sulfates leached from the tanks which received equivalent amounts of CaO and $CaCO_3$. It might thus be assumed that more engendered sulfuric acid was neutralized by the heavy carbonate treatments than by those of the corresponding caustic applications. However, since the solubility of $CaSO_4$ in water solutions of $Ca(OH)_2$ is decidedly less than in water solutions of $CaCO_3$, it does not necessarily follow that the sulfofication of native organic sulfur induced by the carbonate was greater than that induced by the hydrate. Certain unpublished data obtained by the writer have demonstrated that when sulfate salts are applied with excessive amounts of CaO, the amount of sulfur leached as sulfate is very small. This point may be considered more fully when complete carbonation shall have taken place.

Nitrification. The leachings of nitrates also have been determined periodically. The amounts of lime utilized in neutralizing the nitric acid generated represent appreciable and differential aggregates. In the final balancing of leachings and residual lime, these variations also will be considered and reported as a special phase of the study.

Solubilities of $Ca(OH)_2$ *and* $CaCO_3$. The total amount of lime leached from each tank is determined annually by analysis of a composite of the several separate leachings. In addition, the hydrate and carbonate contents are determined periodically by double titration of the separate leachings. The 32 and 100-ton burnt lime tanks continue to yield leachings strongly impregnated with $Ca(OH)_2$ after 4 years of exposure and these leachings carry away a great deal more lime than do those obtained from the carbonate

checks. Since an abundance of hydrated lime remains in the 32 and 100-ton CaO tanks, it cannot be assumed that the leached hydrate would have undergone carbonation, had it not been removed by leaching. Therefore, the several $Ca(OH)_2$ leachings cannot be calculated to $CaCO_3$ and added to the residual $CaCO_3$ in the soil of the respective tanks. Table 31 shows, in the case of the surface soil tanks, losses of 3603, 3566 and 3574 pounds per acre of total lime, calculated as $CaCO_3$, from the 8, 32 and 100-ton $CaCO_3$ tanks,

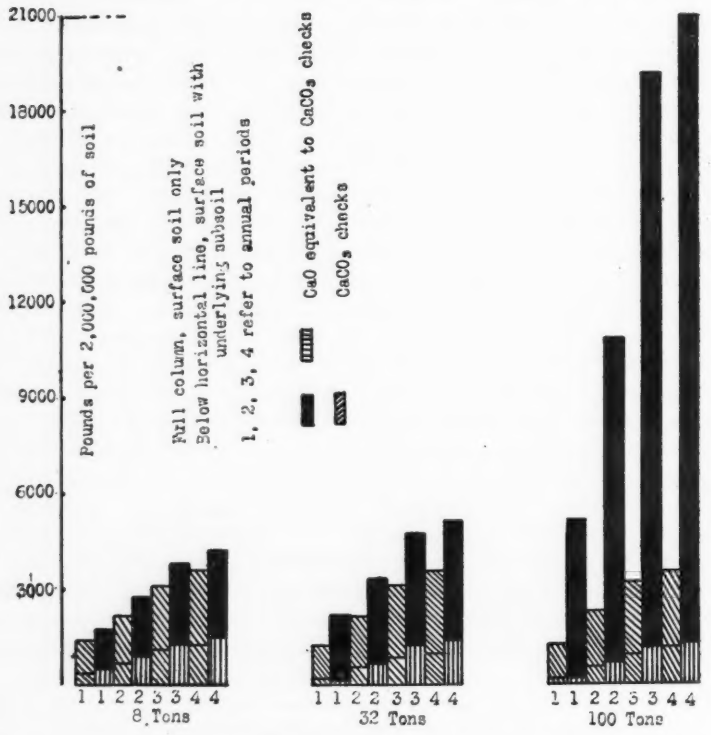

FIG. 4. TOTAL LIME SALTS, AS $CaCO_3$ EQUIVALENCE, LEACHED FROM LYSIMETERS DURING THE INITIAL 4 YEARS OF THE EXPERIMENT (TABLE 31)

respectively. These figures show a remarkable concordance. They demonstrate that with a sufficient surface offered by applied carbonate, the amount of application does not determine the extent of loss. This apparently is controlled rather by the concentration of the carbonated water content of the soil and its period of contact with the carbonate present. When these leachings are compared to the losses from the chemically equivalent CaO tanks without subsoil, we find a considerable variation between the outgo

TABLE 31

Amounts of calcium salts, calculated as $CaCO_3$, in leachings from oxide treatments, as compared to leachings from chemically equivalent carbonate checks during the first 4 years subsequent to applications

TANK NUMBER	TREATMENT		SUBSOIL	TOTAL VOLUME-WEIGHT OF ANNUAL LEACHINGS				CALCIUM-CARBONATE-EQUIVALENCES OF LIME SALTS LEACHED														
								1914–1915			1915–1916			1916–1917			1917–1918			Total for four years 1914–1918		
				1914 to 1915	1915 to 1916	1916 to 1917	1917 to 1918	Per liter	Per tank	Per 2,000,000 pounds of soil	Per liter	Per tank	Per 2,000,000 pounds of soil	Per liter	Per tank	Per 2,000,000 pounds of soil	Per liter	Per tank	Per 2,000,000 pounds of soil	Per liter	Per tank	Per 2,000,000 pounds of soil
	tons			*kgm.*	*kgm.*	*kgm.*	*kgm.*	*gm.*	*gm.*	*lbs.*	*gm.*	*gm.*	*lbs.*	*gm.*	*gm.*	*lbs.*	*gm.*	*gm.*	*lbs.*	*gm.*	*gm.*	*lbs.*
1	CaO	8	None	69.7	136.8	170.1	81.5	0.5750	40.078	1767	0.1760	24.077	1062	0.1345	22.878	1009	0.1241	10.114	446	1.0096	97.147	4,284
3	$CaCO_3$	8	None	74.4	116.7	165.6	86.5	0.4285	31.880	1406	0.1615	18.847	831	0.1250	20.700	913	0.1187	10.268	453	0.8337	81.695	3,603
8	CaO	32	None	79.8	113.9	167.0	71.9	0.6161	49.165	2167	0.2500	28.475	1255	0.1840	30.728	1354	0.1509	10.850	478	1.2010	119.218	5,254
10	$CaCO_3$	32	None	81.5	118.5	181.6	76.8	0.3643	29.690	1309	0.1570	18.605	820	0.1275	23.154	1020	0.1232	9.462	417	0.7720	80.911	3,566
15	CaO	100	None	79.2	107.4	150.7	45.4	1.4821	117.382	5176	1.2090	129.847	5725	1.2350	186.115	8206	0.8196	37.210	1641	4.7457	470.559	20,748
17	$CaCO_3$	100	None	68.5	104.1	163.7	66.5	0.4232	28.989	1278	0.2175	22.642	998	0.1265	20.708	913	0.1313	8.731	385	0.8985	81.070	3,574
22	CaO	8	1 ft. clay	73.2	121.8	173.7	89.5	0.1553	11.368	501	0.0760	9.257	408	0.0535	9.293	410	0.0500	4.475	197	0.3348	34.393	1,516
24	$CaCO_3$	8	1 ft. clay	76.6	120.4	180.7	82.0	0.1035	7.928	350	0.0660	7.946	350	0.0545	9.848	434	0.0482	3.952	174	0.2722	29.674	1,308
29	CaO	32	1 ft. clay	73.2	108.9	157.3	75.9	0.0411	3.009	133	0.1185	12.905	569	0.0795	12.505	551	0.0536	4.068	179	0.2927	32.487	1,432
31	$CaCO_3$	32	1 ft. clay	72.3	110.4	173.1	85.3	0.0714	5.162	228	0.0730	8.059	355	0.0410	7.097	313	0.0393	3.355	148	0.2247	23.673	1,044
36	CaO	100	1 ft. clay	87.5	121.5	163.1	82.4	0.0411	3.596	159	0.0945	11.482	506	0.0640	10.438	460	0.0553	4.557	201	0.2549	30.073	1,326
38	$CaCO_3$	100	1 ft. clay	54.7	104.3	165.4	80.2	0.0714	3.906	172	0.0840	8.761	386	0.0475	7.857	346	0.0670	5.373	237	0.2699	25.897	1,141
45	Blank		1 ft. clay			165.5	69.2							0.0195	3.227	142	0.0134	0.927	*41	*0.0329	*4.154	*183
46	Blank		None			192.4	109.6							0.0330	6.349	280	0.0232	2.543	*112	*0.0562	*8.892	*392

* For 2 years only.

from equivalent applications of CaO and $CaCO_3$, at the rates of 32 and 100 tons. The 8-ton treatments of CaO gave a total loss of 4284 pounds of lime, calculated as $CaCO_3$ for the 4 years, as against 3603 pounds for its carbonate-equivalent check. The 32-ton CaO treatments lost 5254 pounds of $CaCO_3$ as against 3566 pounds for its carbonate-equivalent check; while the 100-ton CaO tank underwent an aggregate lime loss equivalent to 20,748 pounds of $CaCO_3$ as against 3574 pounds for its carbonate check.

Influence of subsoil. The foregoing losses were obtained by direct leachings from the surface soil without any estoppage by underlying subsoil. Were the correction of leached lime to be applied to residual carbonates, the amounts lost from the soil underlaid by subsoil would have to be assumed to be equivalent to those lost where there was no subsoil. The underlying clay subsoil has estopped a large amount of the lime which has passed from the surface soil and it cannot be assumed that the subsoil is saturated with reference to its tendency to absorb lime, until the leachings from the surface soil alone and those underlaid by subsoil are closely approximate in concentration. The total loss of lime, calculated as $CaCO_3$, during the 4-year period is 4284 pounds per acre for the surface soil alone as compared to 1516 pounds for the corresponding treatment of CaO at the rate of 8 tons per acre, where no subsoil was present; while the corresponding $CaCO_3$ checks gave $CaCO_3$-equivalent losses of 3603 and 1308 pounds, respectively. From the 32-ton CaO treatments, the losses of lime in terms of $CaCO_3$ per acre were 5254 pounds for the surface soil alone, as against 1432 pounds for the surface soil plus subsoil tank, while the corresponding carbonate treatments gave 3566 pounds and 1044 pounds, respectively, for surface soil only and soil underlaid by subsoil. Again, the surface soil treated with CaO at the rate of 100 tons per acre gave a $CaCO_3$-equivalent leaching of 20,748 pounds as against but 1326 pounds where the subsoil intervened; while the corresponding $CaCO_3$ checks gave only 3574 pounds for the shallow tank and but 1141 pounds for the deep tank containing both soil and subsoil.

It is thus apparent, that in an effort to effect a final balance when all hydrate shall have disappeared, the summation of data may be so utilized as to leave for determination by process of elimination, only the factor of absorption. As before mentioned the persistency of the hydrate has resulted in a constant contact between a strong $Ca(OH)_2$ solution, as contrasted with a dilute solution of $CaCO_3$ in weakly carbonated water, and it may be anticipated that the amounts of lime absorbed from the oxide admixtures will be shown to be considerably in excess of those absorbed from the carbonate treatments. From the determined residual carbonate content of the soil in each shallow tank, when all hydrate shall have disappeared, together with the known amounts and forms of lime leached, it will be possible by direct application of analyses to arrive at definite conclusions with reference to the different effects of $Ca(OH)_2$ and $CaCO_3$ upon the extent of absorption of CaO by the surface soil. However, in interpreting the data obtained from the subsoil

tanks, it will be necessary to assume that the leachings from the surface soil are equivalent to those from the respective identical treatments, where no subsoil was present to take up any of the lime which has passed through the surface soil. If this assumption is permissible, the extent of absorption effected by the subsoil may also be determined by difference, at a later period.

Until it shall be possible to make complete calculations, the pounds per acre data for the 32 and 100-ton treatments, as given in tables 27 to 30, inclusive, may be considered as being approximate with a tendency to appear higher than the real.

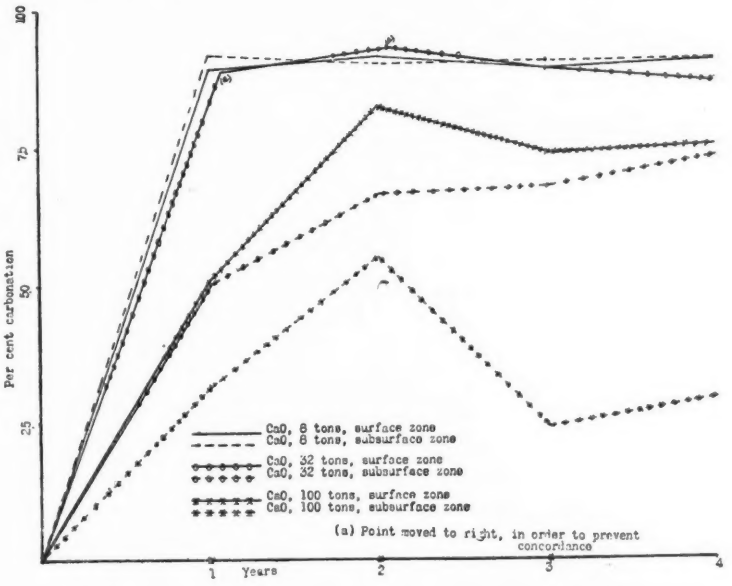

FIG. 5. CARBONATION OF CaO TREATMENTS IN SOIL SURFACES AND SUBSURFACES DURING 4 YEARS' EXPOSURE IN LYSIMETERS (TABLES 32 TO 35)

Carbonation of CaO *treatments effected in soil surfaces and subsurfaces during 4 years' exposure in lysimeters*

At the end of 1, 2, 3, and 4-year periods after placing, samples were taken from the upper and lower portions of the heavily treated lime tanks. The $CaCO_3$ checks were sampled in the same manner. As previously stated, treatments were mixed uniformly throughout the whole of the soil when the soils were placed in the tanks. The analyses of the upper and lower strata at the end of the 1, 2, 3, and 4-year periods are given in tables 32 to 35, inclusive. These analyses show uniform carbonate occurrence throughout the full depth

TABLE 32

Comparisons between extent of carbonation in upper half and that in lower half of an acid Cumberland loam soil in field lysimeter tanks, as derived from determinations of residual carbonates, disregarding differential leachings, at the end of 1 year's exposure; checks received chemically equivalent treatments of $CaCO_3$

SOIL WITHOUT SUBSOIL							SOIL WITH 1 FOOT OF CLAY SUBSOIL						
Laboratory number	Tank number	Treatment	Section analyzed	CO_2 in soil	$CaCO_3$ in soil	Carbonation	Laboratory number	Tank number	Treatment	Section analyzed	CO_2 in soil	$CaCO_3$ in soil	Carbonation
				per cent	*per cent*	*per cent*					*per cent*	*per cent*	*per cent*
4162	1	CaO 8 tons	Upper	0.3345	0.7602	91.27	4186	22	CaO 8 tons	Upper	0.3276	0.7218	87.37
4163	1	CaO 8 tons	Lower	0.3504	0.7964	94.25	4187	22	CaO 8 tons	Lower	0.3407	0.7721	91.72
4166	3	$CaCO_3$ 8 tons	Upper	0.3664	0.8327		4190	24	$CaCO_3$ 8 tons	Upper	0.3635	0.8261	
4167	3	$CaCO_3$ 8 tons	Lower	0.3718	0.8450		4191	24	$CaCO_3$ 8 tons	Lower	0.3704	0.8418	
4170	8	CaO 32 tons	Upper	1.9805	4.5011	93.59	4194	29	CaO 32 tons	Upper	1.7853	4.0575	86.09
4171	8	CaO 32 tons	Lower	1.0596	2.4082	50.38	4195	29	CaO 32 tons	Lower	0.9666	2.2877	49.13
4174	10	$CaCO_3$ 32 tons	Upper	2.1161	4.8095		4198	31	$CaCO_3$ 32 tons	Upper	2.0741	4.7139	
4175	10	$CaCO_3$ 32 tons	Lower	2.1033	4.7802		4199	31	$CaCO_3$ 32 tons	Lower	2.0490	4.6568	
4178	15	CaO 100 tons	Upper	3.1991	7.2707	50.44	4202	36	CaO 100 tons	Upper	3.2628	7.1882	50.92
4179	15	CaO 100 tons	Lower	1.8126	4.1195	29.03	4203	36	CaO 100 tons	Lower	1.9658	4.6950	33.12
4182	17	$CaCO_3$ 100 tons	Upper	6.3423	14.4143		4206	38	$CaCO_3$ 100 tons	Upper	6.2118	14.1177	
4183	17	$CaCO_3$ 100 tons	Lower	6.2468	14.1973		4207	38	$CaCO_3$ 100 tons	Lower	6.2238	14.1450	

TABLE 33

Comparisons between extent of carbonation in upper half and that in lower half of an acid Cumberland loam soil in field lysimeter tanks, without underlying subsoil, as derived from determinations of residual carbonates, disregarding differential leachings, at the end of 2 years' exposure; checks received chemically equivalent treatment of $CaCO_3$

SOIL WITHOUT SUBSOIL							SOIL WITH 1 FOOT OF CLAY SUBSOIL						
Laboratory number	Tank number	Treatment	Section analyzed	CO_2 in soil	$CaCO_3$ in soil	Carbonation	Laboratory number	Tank number	Treatment	Section analyzed	CO_2 in soil	$CaCO_3$ in soil	Carbonation
				per cent	*per cent*	*per cent*					*per cent*	*per cent*	*per cent*
4596	1	CaO 8 tons	Upper	0.2936	0.6673	94.7	4620	22	CaO 8 tons	Upper	0.2833	0.6552	91.4
4597	1	CaO 8 tons	Lower	0.3200	0.7274	91.3	4621	22	CaO 8 tons	Lower	0.3104	0.7055	91.2
4600	3	$CaCO_3$ 8 tons	Upper	0.3101	0.7048		4624	24	$CaCO_3$ 8 tons	Upper	0.3153	0.7166	
4601	3	$CaCO_3$ 8 tons	Lower	0.3506	0.7968		4625	24	$CaCO_3$ 8 tons	Lower	0.3404	0.7736	
4604	8	CaO 32 tons	Upper	1.9398	4.4086	98.5	4628	29	CaO 32 tons	Upper	1.8731	4.2570	90.3
4605	8	CaO 32 tons	Lower	1.3394	3.0441	65.5	4629	29	CaO 32 tons	Lower	1.5826	3.5968	77.0
4608	10	$CaCO_3$ 32 tons	Upper	2.0139	4.5770		4632	31	$CaCO_3$ 32 tons	Upper	2.0739	4.7136	
4609	10	$CaCO_3$ 32 tons	Lower	2.0430	4.6432		4633	31	$CaCO_3$ 32 tons	Lower	2.0564	4.6736	
4612	15	CaO 100 tons	Upper	5.0658	11.5132	80.7	4636	36	CaO 100 tons	Upper	5.2273	11.8780	83.3
4613	15	CaO 100 tons	Lower	2.8516	6.4809	45.5	4637	36	CaO 100 tons	Lower	3.8679	8.7907	63.8
4616	17	$CaCO_3$ 100 tons	Upper	6.2765	14.2648		4640	38	$CaCO_3$ 100 tons	Upper	6.2747	14.2607	
4617	17	$CaCO_3$ 100 tons	Lower	6.2665	14.2420		4641	38	$CaCO_3$ 100 tons	Lower	6.0628	13.7791	

TABLE 34

Comparisons between extent of carbonation in upper half and that in lower half of an acid Cumberland loam soil in field lysimeter tanks as derived from determinations of residual carbonates, disregarding differential leachings, at the end of 3 years' exposure; checks contained chemically equivalent treatments of $CaCO_3$

SOIL WITHOUT SUBSOIL							SOIL WITH 1 FOOT OF CLAY SUBSOIL						
Laboratory number	Tank number	Treatment	Section analyzed	CO_3 in soil	$CaCO_3$ in soil	Carbonation	Laboratory number	Tank number	Treatment	Section analyzed	CO_3 in soil	$CaCO_3$ in soil	Carbonation
				per cent	*per cent*	*per cent*					*per cent*	*per cent*	*per cent*
4894	1	CaO 8 tons	Upper	0.247	0.562	88.2	4918	22	CaO 8 tons	Upper	0.247	0.562	91.8
4895	1	CaO 8 tons	Lower	0.316	0.719	97.3	4919	22	CaO 8 tons	Lower	0.284	0.646	85.8
4898	3	$CaCO_3$ 8 tons	Upper	0.280	0.637		4922	24	$CaCO_3$ 8 tons	Upper	0.269	0.612	
4899	3	$CaCO_3$ 8 tons	Lower	0.325	0.739		4923	24	$CaCO_3$ 8 tons	Lower	0.331	0.753	
4902	8	CaO 32 tons	Upper	1.682	3.823	89.5	4926	29	CaO 32 tons	Upper	1.635	3.716	86.8
4903	8	CaO 32 tons	Lower	1.241	2.821	59.3	4927	29	CaO 32 tons	Lower	1.560	3.546	75.5
4906	10	$CaCO_3$ 32 tons	Upper	1.878	4.269		4930	31	$CaCO_3$ 32 tons	Upper	1.884	4.282	
4907	10	$CaCO_3$ 32 tons	Lower	2.095	4.762		4931	31	$CaCO_3$ 32 tons	Lower	2.066	4.696	
4910	15	CaO 100 tons	Upper	4.149	9.430	69.7	4934	36	CaO 100 tons	Upper	4.477	10.176	76.4
4911	15	CaO 100 tons	Lower	1.385	3.148	21.6	4935	36	CaO 100 tons	Lower	1.551	3.525	25.2
4914	17	$CaCO_3$ 100 tons	Upper	5.953	13.530		4938	38	$CaCO_3$ 100 tons	Upper	5.859	13.316	
4915	17	$CaCO_3$ 100 tons	Lower	6.417	14.584		4939	38	$CaCO_3$ 100 tons	Lower	6.147	13.970	

TABLE 35

Comparisons between extent of carbonation in upper half and that in lower half of an acid Cumberland loam soil in field lysimeter tanks, as derived from determinations of residual carbonates, disregarding differential leachings, at the end of 4 years' exposure; checks contained chemically equivalent treatments of $CaCO_3$

SOIL WITHOUT SUBSOIL							SOIL WITH 1 FOOT OF CLAY SUBSOIL						
Laboratory number	Tank number	Treatment	Section analyzed	CO_2 in soil	$CaCO_3$ in soil	Carbonation	Laboratory number	Tank number	Treatment	Section analyzed	CO_2 in soil	$CaCO_3$ in soil	Carbonation
				per cent	*per cent*	*per cent*					*per cent*	*per cent*	*per cent*
5389	1	CaO 8 tons	Upper	0.116	0.264	84.9	5413	22	CaO 8 tons	Upper	0.266	0.605	98.2
5390	1	CaO 8 tons	Lower	0.146	0.332	91.2	5414	22	CaO 8 tons	Lower	0.299	0.680	103.8*
5393	3	$CaCO_3$ 8 tons	Upper	0.137	0.311		5417	24	$CaCO_3$ 8 tons	Upper	0.271	0.616	
5394	3	$CaCO_3$ 8 tons	Lower	0.160	0.364		5418	24	$CaCO_3$ 8 tons	Lower	0.288	0.655	
5397	8	CaO 32 tons	Upper	1.664	3.782	83.9	5421	29	CaO 32 tons	Upper	1.746	3.968	89.3
5398	8	CaO 32 tons	Lower	1.265	2.875	61.3	5422	29	CaO 32 tons	Lower	1.733	3.938	84.4
5401	10	$CaCO_3$ 32 tons	Upper	1.983	4.507		5425	31	$CaCO_3$ 32 tons	Upper	1.955	4.443	
5402	10	$CaCO_3$ 32 tons	Lower	2.063	4.689		5426	31	$CaCO_3$ 32 tons	Lower	2.054	4.668	
5405	15	CaO 100 tons	Upper	5.318	12.086	85.9	5429	36	CaO 100 tons	Upper	3.800	8.636	62.4
5406	15	CaO 100 tons	Lower	2.036	4.627	33.7	5430	36	CaO 100 tons	Lower	1.452	3.300	23.8
5409	17	$CaCO_3$ 100 tons	Upper	6.194	14.076		5433	38	$CaCO_3$ 100 tons	Upper	6.094	13.850	
5410	17	$CaCO_3$ 100 tons	Lower	6.050	13.750		5434	38	$CaCO_3$ 100 tons	Lower	6.110	13.886	

* Not included in graph average.

of the soil which received CaO at the rate of 8 tons of CaO per 2,000,000 pounds of soil. The analyses do not, however, necessarily establish the fact that carbonation of the 8-ton treatments was effected with the same rapidity in the two strata. While the extent of carbonation was practically the same in the two strata after 1 year of exposure, it is quite possible that the carbonation effected within that interval may have been effected much more rapidly in one stratum than in the other.

The results obtained from the 32-ton tanks show a decided difference in the amounts of carbonate produced in the surface 4 inches, as compared to the amounts found in the lower 4-inch stratum. At the end of the first year about nine-tenths of the CaO of the upper 4 inches had been converted to $CaCO_3$ while about one-half of the lime in the lower stratum had been carbonated. At the end of the second year about 95 per cent of the upper stratum had undergone carbonation while the carbonation effected in the lower stratum amounted to about 70 per cent.

The results obtained from the 100-ton treatments are in accord with those secured from the 32-ton applications, in that much more extensive carbonation took place in the upper stratum than in the lower. About one-half of the lime present in the upper layer had undergone reversion to carbonate at the end of one year's exposure, while about four-fifths had become carbonated at the end of the second year. In the case of the lower stratum, about 30 per cent of the caustic form had been neutralized at the end of the first year of exposure, while at the end of the second year about one-half of the applied lime still remained in the caustic form. The distinctly greater carbonation effected in the upper stratum of each of the 32 and 100-ton tanks indicated that the CO_2 of the soil atmosphere of these tanks suffered reduction to a minimum. Hence, relatively greater infusion of atmosphere into the upper layer was responsible for the more extensive carbonation there effected. Moreover, the upper stratum would extract the CO_2 contained in rainfall, and perhaps dew as well. In other words, apparently the excessive caustic treatments effectuated conditions of partial sterilization, thereby necessitating dependence primarily upon infusion of atmosphere and precipitation as a source of CO_2 for the carbonation of CaO. This phase of the problem was then considered.

Influence of heavy treatments of CaO *upon the occurrence of atmospheric* CO_2 *in tank soils*

It seemed possible that, in the soils relatively dry as a result of the marked physical effect of the excessive lime treatments, causticity might persist because of protective action of $CaCO_3$ in spite of an abundance of atmospheric CO_2 in the soil. Again, the possibility of partial sterilization above mentioned seemed germane. Therefore, the atmosphere of the 12 tanks was analyzed at various periods during the 4 years. The samples were drawn off

from the bottom by means of the block-tin drainage outlets. Five hundred cubic centimeters were first drawn off and discarded in order to insure absence of error introduced by diffusion of atmosphere into the block-tin tubes. At first 500-cc. samples were then drawn off by means of a mercury siphon, dried and absorbed in $Ba(OH)_2$. Later the volumes of samples were increased to 2 litres and then 3 litres. Corrections were then made for observed temperature and pressure and later for moisture vapor, when a water siphon was used in place of mercury. The results are recorded in table 36.

The analyses of these atmospheres show a decided tendency of caustic lime to effect both an initial and a continued depletion of atmospheric CO_2. It does not appear, however, that the excess of $CaCO_3$ has resulted in a diminution of the CO_2 of the soil atmosphere. The 8-ton treatment had become almost, if not completely, carbonated in less than one year and it would seem, therefore, that in the absence of caustic lime, and with a probable increase of available nutrients, recovery from any possible partial sterilization would have occurred subsequent to the initial year.

In a comprehensive biological study of five soils, Hutchinson and MacLennan (38) used bacteria counts to determine the sterilizing effect of lime. They used amounts of CaO varying from 0.1 per cent to 1.0 per cent and concluded that partial sterilization follows in the wake of applications in excess of 0.3 per cent. They note, however, a somewhat rapid return to normal numbers. The complete carbonation of the burnt lime and the return to normality were apparently somewhat coincident. As judged by atmospheric-CO_2 content, the consistently smaller amounts of CO_2 found in the 8-ton treatments point to the conclusion that the full restoration of biological activities had not ensued even after a period of two years. There appeared one additional possibility which was suggested by the results obtained by Russell and Appleyard (58). These investigators found a marked difference between the CO_2 content of the soil atmosphere and the CO_2 absorbed by the surface moisture film. Russell and Appleyard observed an increase in pressure, upon standing, in the atmosphere above a moist soil which had been subjected to thorough evacuation. This was found to be due to the retarded evolution of a film-absorbed gas which proved to be almost pure CO_2. The absorption apparently was a surface phenomenon.

Treatment with caustic lime in amounts equivalent to 8 tons effected a marked flocculation of colloidal material which would naturally decrease the effective surface. It is, therefore, possible that bacterial activities may have returned to normal and that the lesser CO_2 content was due to physical alteration of the soil structure, and a resultant disturbance of the initial equilibrium between CO_2 content of atmosphere, free water and film water. The results are not surprising in the case of 32- and 100-ton treatments. The continued presence of so much uncarbonated lime would be expected to eliminate atmospheric carbonic acid gas and maintain a condition of partial sterility with minimum evolution of CO_2.

TABLE 36

Atmospheric CO_2 content of CaO and $CaCO_3$-treated loam soil of tanks at periods between 1914 and 1918; results calculated to per cent of CO_2 by weight, dry air, at 0° C. and 760 mm. pressure

DATE OF SAMPLING OF ATMOSPHERE	SOIL WITHOUT SUBSOIL							SOIL WITH 1 FOOT OF CLAY SUBSOIL						
	Treatment							Treatment						
	CaO 8 tons	$CaCO_3$ = CaO 8 tons	CaO 32 tons	$CaCO_3$ = CaO 32 tons	CaO 100 tons	$CaCO_3$ = CaO 100 tons	Blank	CaO 8 tons	$CaCO_3$ = CaO 8 tons	CaO 32 tons	$CaCO_3$ = CaO 32 tons	CaO 100 tons	$CaCO_3$ = CaO 100 tons	Blank
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
June 30, 1916	0.262	0.328	0.046	0.452	0.045	0.405		0.438	0.576	0.094	0.448	0.096	0.629	
July 14, 1916	0.269	0.309	0.045	0.219	0.045	0.223		0.332	0.386	0.092	0.266	0.088	0.350	
October 12, 1916	0.147	0.169	0.043	0.191	0.000	0.170		0.126	0.169	0.043	0.168	0.022	0.166	
April 18, 1917	0.179	0.179	0.000	0.271	0.047	0.217	6.147	0.271	0.503	0.139	0.813	0.093	0.604	0.767
May 18, 1917	0.000	0.022	0.000	0.023	0.000	0.160	0.159	0.137	0.207	0.046	0.160	0.046	0.023	0.545
September 19, 1917	0.245	0.667	0.134	0.313	0.091	0.407	0.837	0.293	0.159	0.249	0.204	0.113	0.453	0.272
May 15, 1918	0.134	0.173	0.038	0.211	0.026	0.313		0.070		0.237	0.147		0.684	
August 31, 1918	0.133	0.146	0.013	0.139	0.000	0.186	0.238	0.152	0.300	0.118	0.179	0.113	0.252	0.173
Average	0.171	0.249	0.040	0.227	0.032	0.260	1.845	0.227	0.329	0.127	0.298	0.082	0.395	0.439

An additional point worthy of notation is suggested by the data of table 36. These data indicate that the atmosphere of the tanks underlaid by subsoil was considerably richer in CO_2 than was that of the soils without underlying subsoil. The atmosphere was sampled in both cases by aspiration from the bottom by means of the drainage outlets, and only small initial withdrawals were required to effect a constant composition. This constant was maintained after drawing quantities equivalent to a large multiple of the volume used for analysis. In the case of the subsoil tanks it follows, then, that the atmosphere of the dense clay of the subsoil was drawn off rather than the atmosphere of the surface soil. From this it appears that the atmosphere of the dense clay subsoil, almost free of organic matter, is richer in CO_2 than is the atmosphere of the surface soil. This suggests two possibilities. Selective absorption, or rather surface condensation, of CO_2 may be evidenced. Again, the lower temperature and the probable increased pressure characteristic of the subsoil may result in a more highly carbonated soil water. Reduction of pressure, incident to aspiration, would tend to effect release of CO_2 thus held in solution. Furthermore, the heavily lime-treated surface soil yields a leaching strongly impregnated with bicarbonate of lime, and this salt is still being absorbed by the subsoil, with a liberation of CO_2.

TUMBLER EXPERIMENTS TO DETERMINE RAPIDITY OF THE CARBONATION OF HYDRATED LIME EXPOSED ON THE SURFACE OF SOIL, AS COMPARED TO THAT EFFECTED UPON HYDRATED LIME INCORPORATED WITH THE SOIL

The data obtained from the foregoing lysimeter studies show that carbonation of burnt lime was more extensive in the upper half than in the lower half of the surface soil, when large amounts were simultaneously and uniformly mixed throughout the entire 8 inches of Cumberland loam. The nature of the experiments, and the equipment required, together with the character of certain other involved comparisons necessitated the thorough mixing of soil and treatments at the beginning of the experiments. This was true for both the leaching tanks and the naturally drained cylinders. These two series of experiments did not, therefore, permit of comparison between the rate of carbonation of burnt or hydrated lime applied to and left upon the surface, and that obtained by incorporating the oxide or hydrate in the soil. This phase of the problem was then attacked under the following conditions of laboratory control. Glass tumblers $4\frac{1}{2}$ inches high were used as containers. Two soils, a Volusia silt loam and a Dunkirk clay loam, were used in this work. Both of these soils are of glacial till origin and both were obtained in the near vicinity of the Cornell Station Farm. Both soils were gray in color and acid to litmus paper.

It was, of course, necessary to take into consideration the fact that if acid soils were used, a comparison could not be drawn quantitatively between

the carbonation of a definite amount of burnt lime applied and mixed throughout the soil and the carbonation resulting from an equal amount of burnt lime applied to and left on the soil surface. With an admixture of acid soil and lime there would occur absorption and fixation of lime which could not then be directly carbonated. With many soils the entire application of economical amounts of CaO thus applied, might be quickly absorbed from the hydrate by acid-reacting soil materials, leaving none to undergo carbonation.

In making dry admixtures, however, this would not hold true. Nor would there be appreciable absorption from undisturbed surface contact of lime with relatively small soil surface in the case of moistened but unleached acid soils. It was, therefore, necessary to eliminate or minimize the question of lime absorption by means of preliminary treatment of the acid soils to be utilized in the experiments. The plan adopted was as follows. Freshly sampled soils were brought to the laboratory, spread thinly, and permitted to air-dry. They were then sifted through a 2.5-mm. sieve and thoroughly mixed in order to insure uniformity of composition. The air-dry soils were next mixed with dry carbonated-water-treated precipitated $CaCO_3$ and then wetted to the consistency of soupy paste in galvanized iron containers. Two hundred and twenty-five pounds of Volusia soil and 612 gm. of $CaCO_3$ were mixed and moist contact continued with frequent stirrings for 18 days. Two hundred and thirty-four pounds of the Dunkirk soil and 637 gm. of $CaCO_3$ were treated, as was the Volusia silt loam. The Dunkirk clay was in moist contact with an excess of $CaCO_3$ for a period of 38 days. The amounts of $CaCO_3$ used represented field treatments equivalent to 12,000 pounds per acre 2,000,000 pounds of soil. Guided by lime-requirement determinations, it was empirically determined that this amount would insure neutralization of the immediate lime requirement, and also furnish a determinable excess of carbonate. At the end of the specified periods of contact the soils were poured out in thin layers on concrete floors and permitted to air-dry with frequent rakings. The alkaline air-dried soil was again passed through a 2.5-mm. sieve and thoroughly mixed. The flocculation effected by the $CaCO_3$ treatment produced a soil finely powdered as compared to the initial soil. The $Ca(OH)_2$ treatments were based upon *surface areas*, rather than upon the weight per acre of any definite depth. Applications at rates of *4 and 8 tons per acre surface* were then computed into grams per area of glass containers. A definite quantity of soil was used throughout giving a constant depth of $3\frac{1}{2}$ inches. In one series the lime was thoroughly mixed to this depth while in another series the lime was applied to the surface and evenly spread. At sampling periods the surface treatments were mixed with the soil. They were then sifted through a 1-mm. sieve, bottled and analyzed in a manner similar to that followed in the case of treatments where soil and lime were in intimate contact throughout.

The plan of treatment included consideration of the moisture factor, as compared to air-dry conditions; and the protective action of a sand mulch

to reduce aeration as compared with unrestricted exposure. An attempt was also made to insure permanent sterile conditions, during exposure, thus eliminating nitrification and generation of CO_2, and thus to differentiate between carbonation effected by atmospheric CO_2 and that produced biologically within the soil.

In considering the question of an antiseptic which would not involve absorption and various chemical transformations, *a priori* considerations resulted in the elimination of all the known effective materials except formaldehyde. Nor was this substance assumed to be ideal for the purpose intended. The anticipations and precautions attendent upon its use will be considered in the discussion of results. Twenty per cent formaldehyde, acid-free, was used.

In order that pore space might be as nearly constant and comparable as possible, in the dry conditions and in the two moist treatments, it was determined empirically to what volume the soil should be compacted so that expansive and contractive tendencies of wetting would be practically neutralized. This degree of compactness would probably be less conducive to oxidation and intra soil aeration and resultant carbonation of the hydrated lime included in the soil mass, than would be the case were the same soils freshly tilled in the field. It was necessary, however, to anticipate the compacting which would result from repeated wettings in order to effect comparable compactness in the three conditions maintained. Furthermore. there was necessarily less exposure to wind movement in the indoor exposure studies than would have been the case in the field. In studying the factors influencing carbonation it was, therefore, intended to effect conditions which would be comparably correct, rather than to secure results which, in actual rapidity of carbonation, would be in close harmony with field conditions.

The Volusia and Dunkirk soils were not run simultaneously. The former was exposed in a well ventilated greenhouse from September 1, 1915, to December 8, 1915. The latter was exposed in a large attic room from December 29, 1915, to March 22, 1916. The glass containers were embedded in an improvised soil of black well leached cinders. The artificial soil was leached to prevent any carbonate contamination by cinder dust or particles becoming incorporated in the treated soils. Each specified treatment was applied in quadruplicate and one of the quadruplicates was taken at each of the designated intervals. When sampled the entire content of each tumbler was turned out into agate-ware pans, immediately placed in electric ovens and dried overnight at 105°C. On removal from the oven, each tumbler's contents were immediately passed through a 1-mm. sieve and thoroughly mixed by rolling. Portions for analyses were then preserved in 8-ounce bottles, sealed with paraffin. The following scheme was carried out in the tumbler exposures:

1. Air-dried soil mixed throughout with $Ca(OH)_2$ at rate of 4 tons of CaO per acre of surface.
2. Air-dried soil and surface application of $Ca(OH)_2$ at the rate of 4 tons of CaO per acre of surface.
3. Same as 1 with an inch of CO_2-free quartz sand as mulch over lime.
2. Same as 2 with an inch of CO_2-free quartz sand as mulch over lime.
5. Air-dried soil mixed throughout with $Ca(OH)_2$ at the rate of 8 tons of CaO per acre of surface.
6. Air-dried soil and surface application of $Ca(OH)_2$ at the rate of 8 tons of CaO per acre of surface.
7. Same as 5 with an inch of CO_2-free quartz sand as mulch over lime.
8. Same as 6 with an inch of CO_2-free quartz sand as mulch over lime.

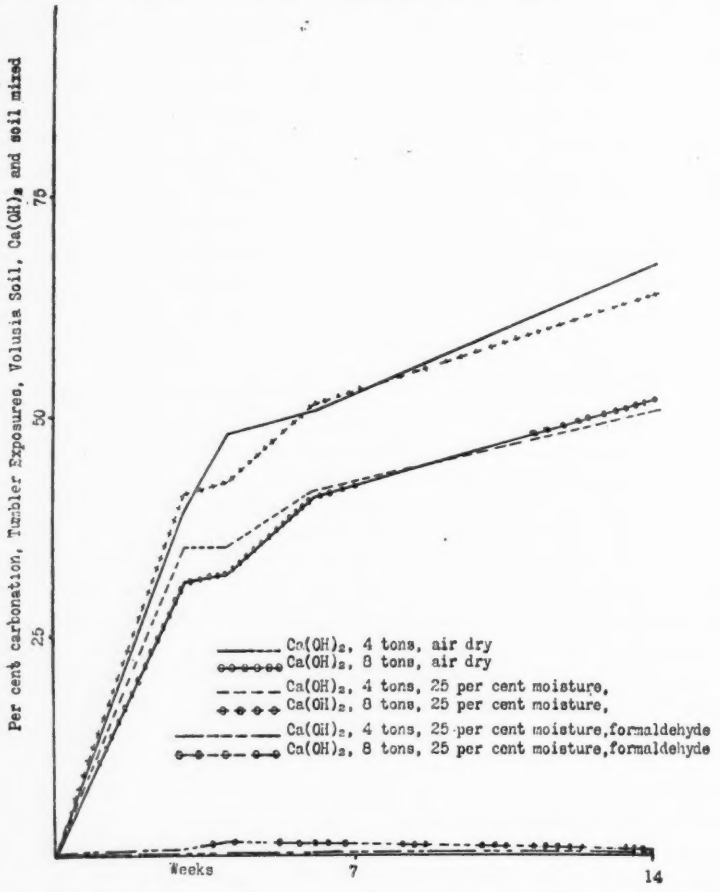
Per cent carbonation, Tumbler Exposures, Volusia Soil, Ca(OH)2 and soil mixed
25
50
75
Weeks
7
14
Ca(OH)2, 4 tons, air dry
Ca(OH)2, 8 tons, air dry
Ca(OH)2, 4 tons, 25 per cent moisture,
Ca(OH)2, 8 tons, 25 per cent moisture,
Ca(OH)2, 4 tons, 25 per cent moisture,formaldehyde
Ca(OH)2, 8 tons, 25 per cent moisture,formaldehyde

FIG. 6. TUMBLER EXPOSURE EXPERIMENTS, VOLUSIA SOIL—$Ca(OH)_2$ AND SOIL MIXED (TABLES 37, 38 AND 39)

TABLE 37

Speed of carbonation of 4 and 8 tons of CaO (*as* $Ca(OH)_2$) *per acre surface when mixed throughout 3½ inches of air-dry alkaline Volusia silt loam, as compared with carbonation of the same amount when applied to and left upon the surface*

PERIOD OF EXPOSURE	METHOD OF TREATMENT															
	CaO 4 tons mixed		CaO 4 tons surface		CaO 4 tons mixed and sand mulch		CaO 4 tons surface and sand mulch		CaO 8 tons mixed		CaO 8 tons surface		CaO 8 tons mixed and sand mulch		CaO 8 tons surface and sand mulch	
	Carbonated		Carbonated		Carbonated		Carbonated		Carbonated		Carbonated		Carbonated		Carbonated	
	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface
weeks																
3	37.9	2769	81.6	5961	31.7	2316	49.3	3601	30.8	4500	85.1	12,433	19.2	2805	25.8	3769
4	47.8	3492	79.8	5829	33.3	2433	61.6	4500	31.7	4631	90.8	13,266	23.8	3477	34.2	4997
6	50.4	3682	82.7	6041	43.1	3148	83.4	6092	40.5	5817	90.9	13,280	29.4	4295	45.8	6591
14	67.3	4916	87.5	6012	56.1	4098	90.7	6625	52.0	7597	92.3	13,485	43.3	6326	62.5	9031

TABLE 38

Speed of carbonation of 4 and 8 tons of CaO (*as* $Ca(OH)_2$) *per acre surface when mixed throughout 3½ inches of alkaline Volusia silt loam maintained at 25 per cent moisture content, as compared with the carbonation of the same amount applied to and left upon the surface*

PERIOD OF EXPOSURE	METHOD OF TREATMENT															
	CaO 4 tons mixed		CaO 4 tons surface		CaO 4 tons mixed and sand mulch		CaO 4 tons surface and sand mulch		CaO 8 tons mixed		CaO 8 tons surface		CaO 8 tons mixed and sand mulch		CaO 8 tons surface and sand mulch	
	Carbonated		Carbonated		Carbonated		Carbonated		Carbonated		Carbonated		Carbonated		Carbonated	
	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface
weeks																
3	41.1	3002	46.3	3382	31.9	2330	31.4	2294	35.1	5128	34.4	5026	23.5	3433	19.7	2788
4	42.3	3090	66.0	4821	40.1	2929	36.2	2644	35.1	5128	34.8	5084	28.6	4178	22.1	3229
8	51.1	3733	83.0	6063	53.4	3901	39.3	2871	41.3	6034	62.1	9073	28.9	4222	22.9	3346
14	63.7	4653	87.4	6385	61.6	4500	74.0	5406	50.4	7363	67.8	9906	41.2	5909	50.9	7436

TABLE 39

Speed of carbonation of 4 and 8 tons of CaO (*as* $Ca(OH)_2$) *per acre when mixed throughout 3½ inches of alkaline Volusia silt loam maintained at 25 per cent moisture content with 20 per cent formaldehyde, as compared with the carbonation of the same amounts when applied to and left upon the surface*

PERIOD OF EXPOSURE	METHOD OF TREATMENT															
	CaO 4 tons mixed		CaO 4 tons surface		CaO 4 tons mixed and sand mulch		CaO 4 tons surface and sand mulch		CaO 8 tons mixed		CaO 8 tons surface		CaO 8 tons mixed and sand mulch		CaO 8 tons surface and sand mulch	
	Carbonated		Carbonated		Carbonated		Carbonated		Carbonated		Carbonated		Carbonated		Carbonated	
	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface
weeks																
3	0	0	15.2	1110	0	0	11.5	840	0.6	88	17.5	2558	1.1	161	9.3	1359
4	0	0	15.6	1140	0	0	18.4	1344	1.5	219	16.9	2479	0.9	131	10.0	1461
6	0	0	13.5	986	0	0	17.9	1308	1.1	161	17.6	2571	1.3	190	12.5	1826
14	0	0	16.8	1227	0	0	12.6	920	0.5	73	19.2	2805	0	0	18.0	2630

After application of the above treatments, four glasses of each treatment were left air-dry, four of each treatment were wetted to 25 per cent moisture content with freshly distilled water and the same number were brought to 25 per cent moisture content with 20 per cent formaldehyde. The glasses containing the wetted treatments were maintained at constant weight by additions of CO_2–free distilled water and 20 per cent formaldehyde, respectively. Plate 3 shows the Dunkirk soil series at the beginning of the experiment.

Carbonation of lime effected in tumbler exposures

The data derived from the tumbler exposure experiments are given in tables 37 to 44, inclusive.

The exposures with the Volusia soil will be first considered. Inspection of table 37 shows that the surface application of $Ca(OH)_2$ carbonated much more rapidly than did the hydrate which was mixed throughout the dry soil, in both 4 and 8-ton treatments. In the dry condition the biological activities would be exceedingly small, and the lime would necessarily draw from the air the CO_2 required for the reversion of the hydrate to the carbonate. Hence, it would be expected that the restricted diffusion of atmosphere into pore spaces would result in less carbonation than would be effected in the case of the surface applications. This is further emphasized by the lesser carbonation which transpired, where diffusion was restricted by appli-

cations of a 1-inch coarse sand mulch. In each case the greatest per cent of carbonation per unit of lime was effected during the initial 3-week interval. In the surface applications, devoid of mulch, about 80 per cent of theoretical carbonation resulted within the first 3 weeks. The reversion to carbonate

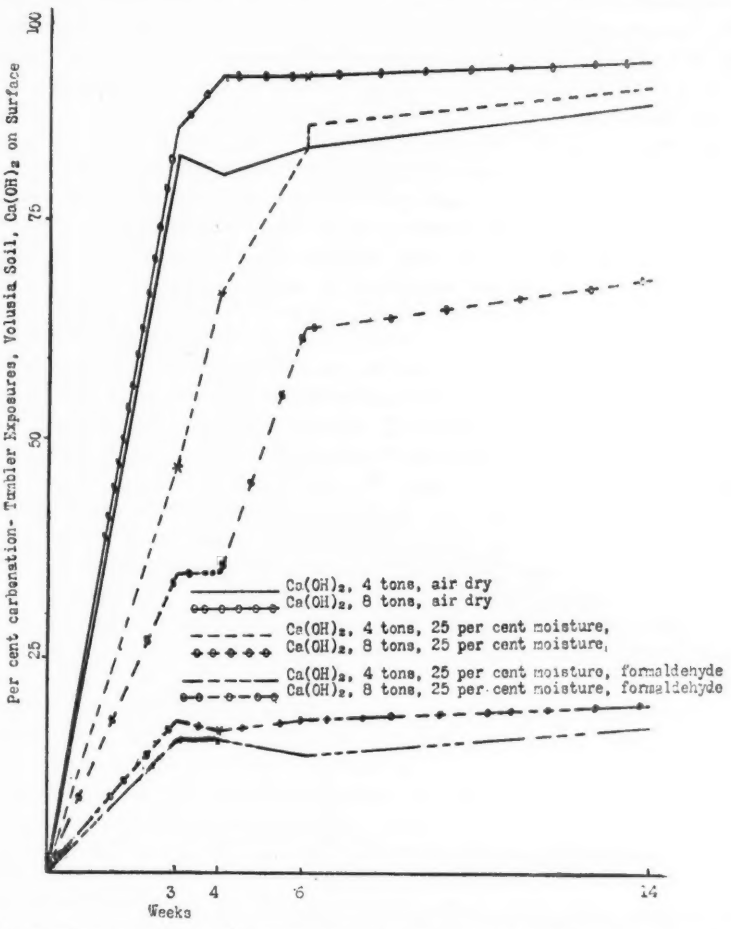

FIG. 7. TUMBLER EXPOSURE EXPERIMENTS, VOLUSIA SOIL—$Ca(OH)_2$ ON SOIL SURFACE (TABLES 37, 38 AND 39)

was slow beyond that time. In those tumblers in which lime was mixed throughout the soil, and also where the mulches were applied, carbonation was slower initially and less ultimately with a more gradual increase, than in the case of the surface applications. In the day treatments the carbo-

nation came to an apparent equilibrium without effecting theoretical carbonation, in the same manner as did the first exposures recorded in table 10.

With the addition of the water, in the tumblers where the moisture content was maintained at 25 per cent, additional factors are involved. The water in this set was added from the top, an air vent being afforded by a small glass tube extending to the bottom of the tumbler. In order to prevent the absorption of the entire amount of water by the upper portion of the soil, thus leaving a dry bottom layer which would pull from the moist strata, the initial wetting was beyond the condition maintained as a constant. This precaution resulted in a mass almost devoid of subsequent cracks. In these wet treatments the surface carbonation was also greater than that found within the soil. The compactness of the soil and the fact that pore space was diminished by the added water, would tend to restrict the infusion of atmosphere into these moist soils. Furthermore, the carbonation of the mixed 4-ton treatments was not materially altered by the presence of the mulch. It would, therefore, appear that the carbonation effected within the body of the soil receiving 4 tons is to be attributed in a large part to the biological evolution of carbon dioxide. On the other hand, however, there occurred the possibility of partial sterilization having been produced. For, while the 4 and 8-ton treatments are not excessive, as surface applications, they assume the proportions of 8 and 16 tons per acre, 7 inches, respectively, when mixed throughout $3\frac{1}{2}$ inches of soil. When we consider the 8-ton treatments, we find a difference. In this case the sand mulch has lessened the extent of reversion of $Ca(OH)_2$ to carbonate, indicating a sterilizing effect and a dependence upon atmospheric infusion as a source of CO_2.

We come now to the tumblers in which formaldehyde was used. In the treatments accorded this set, an endeavor was made to produce and maintain sterile soil conditions, at the same time, permitting free access to atmosphere. A careful preliminary survey of positive antiseptics was made. From such a search it seems impossible to secure a substance which would not introduce errors through either absorption or side reactions. Though difficulties were anticipated, it was decided to use acid-free formaldehyde, diluted 1 to 1. The possibility that the inherent oxidative power of the soils would cause oxidation of formaldehyde to formic acid was considered and determined qualitatively. For this purpose an extra set of treatments and $CaCO_3$ checks were enclosed in rubber-stoppered Erlenmeyer flasks, containing intake and outgo glass tubes to which were sealed glass stopcocks. After a period of some weeks the atmosphere of the sterile $CaCO_3$-treated check flasks was drawn off and found to be heavily impregnated with CO_2. This is further shown in the determination of residual carbonates of the checks after treatment with formaldehyde, as given in table 43. This demonstrated that the formic acid generated had attacked the precipitated carbonate of the preliminary treatment. It may be, however, that acid compounds were generated from contact of amino and amido compounds with formaldehyde. This phe-

nomenon was also demonstrated by analysis of $CaCO_3$-treated tumbler checks, for residual carbonate as shown in table 43.

Spoehr (62) noted that formaldehyde underwent oxidation with the production of formic acid on exposure to the atmosphere. He also noted the formation of a sugar in the presence of $Ca(OH)_2$, even in the dark. Such a condition existed in the mixed moist treatment and it is quite possible that acetic acid may have also been formed from the sugar produced by action of lime upon formaldehyde. Butlerow (9) is cited as having made the same observation. Sadtler and Coblentz (60) state that formaldehyde polymerizes into a white crystalline mass known as para-formaldehyde, and that Fisher observed the formation of an inactive sugar, which he designated as anacrose of the formulum $C_6H_{12}O_6$. Both of these observations were also made in the tumbler studies. Plate 4 shows the accumulation of para-formaldehyde upon the surface of the Volusia soil after 14 weeks. In addition, the capillary rise brought to the soil surface a yellowish syrupy substance, which formed caramel upon heating.

While the efficiency of the formaldehyde was proved by the determined sterility of the 8 tumblers exposed during the 14 weeks, the complications above cited nullified the apparent indications advanced by the determinations of CO_2, as given in table 39. Because of the lack of carbonate increase from the mixed 4-ton treatments and the minute amounts formed in the 8-ton treatments it appears that as fast as the transformation of formaldehyde to formic acid occurred, the free acid was neutralized by the hydrated lime. The surface carbonation shown indicates that the vapor pressure of the formaldehyde was not sufficiently strong to prevent carbonation from the atmosphere. The fluctuations which were carefully checked, may possibly be accounted for by capillary rise of the formic acid or other acids generated near the top of the soil or by the oxidation of the sugar above-mentioned.

Carbonation of $Ca(OH)_2$ *when applied upon surface and when mixed throughout Dunkirk clay loam*

The trend of the results of the exposure of the Dunkirk soil is very similar to that shown in the case of the Volusia. In the dry treatments the carbonation has been more rapid on the surface than in the body of the soil. The protective action of a sand mulch also is well exemplified. In the 4-ton and 8-ton surface applications, with moisture maintained at 25 per cent, the percentage carbonation amounted to 94.5 and 99.2, respectively. In these exposures the successive additions of water, added in maintaining a constant soil moisture supply, were responsible for repeated disruptures of the surface coatings of carbonate, thus permitting almost complete carbonation.

In the case of the moist treatments the same relationships likewise hold. Again, in the treatments to which formaldehyde was added, the acid produced from oxidation, accelerated by extensive surface, has prevented any

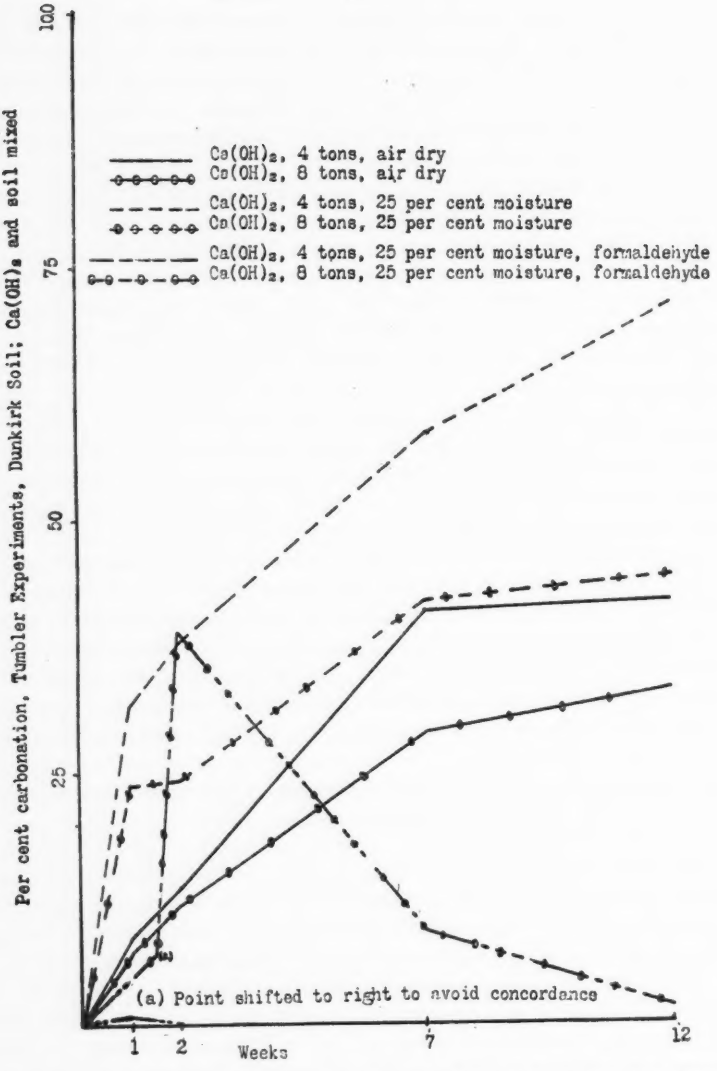
Per cent carbonation, Tumbler Experiments, Dunkirk Soil; Ca(OH)₂ and soil mixed
100
75
50
25
Ca(OH)₂, 4 tons, air dry
Ca(OH)₂, 8 tons, air dry
Ca(OH)₂, 4 tons, 25 per cent moisture
Ca(OH)₂, 8 tons, 25 per cent moisture
Ca(OH)₂, 4 tons, 25 per cent moisture, formaldehyde
Ca(OH)₂, 8 tons, 25 per cent moisture, formaldehyde
(a) Point shifted to right to avoid concordance
1
2
7
12
Weeks

FIG. 8. TUMBLER EXPOSURE EXPERIMENTS, DUNKIRK SOIL—$Ca(OH)_2$ AND SOIL MIXED (TABLES 40, 41 AND 42)

TABLE 40

Speed of carbonation of 4 and 8 tons of CaO (*as* $Ca(OH)_2$) *per acre surface when mixed throughout 3½ inches of air-dry alkaline Dunkirk clay loam, as compared with carbonation of the same amounts applied to and left upon the surface*

PERIOD OF EXPOSURE	METHOD OF TREATMENT															
	CaO 4 tons mixed		CaO 4 tons surface		CaO 4 tons mixed and sand mulch		CaO 4 tons surface and sand mulch		CaO 8 tons mixed		CaO 8 tons surface		CaO 8 tons mixed and sand mulch		CaO 8 tons surface and sand mulch	
	Carbonated		Carbonated		Carbonated		Carbonated		Carbonated		Carbonated		Carbonated		Carbonated	
	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface
weeks																
1	8.6	628	14.0	1023	9.1	665	9.3	679	7.1	1037	7.9	1154	5.2	760	6.9	1008
2	13.3	971	24.2	1768	11.0	804	13.1	957	11.6	1695	17.8	2601	7.5	1096	11.9	1739
7	40.6	2966	56.5	4127	32.5	2374	39.2	2864	28.5	4164	45.6	6662	22.5	3287	28.3	4135
12	41.9	3061	56.5	4127	37.3	2725	53.7	3923	32.8	4792	46.8	6837	29.5	4310	38.8	5669

TABLE 41

Speed of carbonation of 4 and 8 tons of CaO (*as* $Ca(OH)_2$) *per acre surface when mixed throughout 3½ inches of alkaline Dunkirk clay loam maintained at 25 per cent moisture content, as compared with the carbonation of the same amounts when applied to and left upon the surface*

PERIOD OF EXPOSURE	METHOD OF TREATMENT															
	CaO 4 tons mixed		CaO 4 tons surface		CaO 4 tons mixed and sand mulch		CaO 4 tons surface and sand mulch		CaO 8 tons mixed		CaO 8 tons surface		CaO 8 tons mixed and sand mulch		CaO 8 tons surface and sand mulch	
	Carbonated		Carbonated		Carbonated		Carbonated		Carbonated		Carbonated		Carbonated		Carbonated	
	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface
weeks																
1	31.2	2289	64.0	4675	14.4	1052	20.9	1527	23.6	3448	36.1	6,299	20.7	3024	11.5	1,680
2	37.2	2717	83.9	6129	35.6	2601	32.5	2374	24.1	3521	61.8	9,029	20.9	3053	18.3	2,674
7	57.8	4222	85.2	6224	48.1	3514	80.8	5902	41.6	5978	94.6	13,821	27.8	4062	48.8	7,130
12	67.9	4960	94.5	6913	50.5	3689	90.0	6575	43.8	6399	99.2	14,493	36.5	5333	72.3	10,563

TABLE 42

Speed of carbonation of 4 and 8 tons of CaO (*as* $Ca(OH)_2$) *per acre surface when mixed throughout 3½ inches of alkaline Dunkirk clay loam maintained at 25 per cent moisture content with neutral 20 per cent formaldehyde, as compared with carbonation of the same amounts when applied to and left upon the surface*

PERIOD OF EXPOSURE	METHOD OF TREATMENT															
	CaO 4 tons mixed		CaO 4 tons surface		CaO 4 tons mixed and sand mulch		CaO 4 tons surface and sand mulch		CaO 8 tons mixed		CaO 8 tons surface		CaO 8 tons mixed and sand mulch		CaO 8 tons surface and sand mulch	
	Carbonated		Carbonated		Carbonated		Carbonated		Carbonated		Carbonated		Carbonated		Carbonated	
	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface	Per cent	Pounds per acre surface
weeks																
1	0	0	28.0	2045	0	0	8.0	584	7.1	1038	7.5	1096	4.8	701	7.3	1067
2	0.8	58	29.9	2183	0	0	12.2	891	38.2	5582	23.9	3492	4.9	716	9.2	1344
7	0	0	32.2	2352	0	0	28.0	2045	9.2	1344	44.2	6458	4.8	701	14.6	2133
12	0	0	19.0	1388	0	0	22.6	1651	1.6	234	40.5	5917	1.6	234	24.6	3594

consistent or extensive accumulation of carbonate. The foregoing experiments indicate that when burnt lime is left upon the soil surface *in the amounts and of fineness comparable to that used experimentally*, it will carbonate more quickly than when incorporated with or under a dry mulch. The same relationship would appear to hold also if the soils were compacted by rain.

Constancy of checks used in tumbler experiments

In comparing the production of carbonates from the applied hydrates, it was not assumed that the checks would remain constant for a long period under conditions of moist contact. It has been shown that some soils and certain soil constituents, alkaline, sterile, and free of organic matter will continue to evolve CO_2 when left for relatively long periods in contact with $CaCO_3$. For this reason separate checks were used in the work, one set for dry treatments, one for moist treatments and a third for the formaldehyde tumblers.

Some further absorption of calcium appeared to follow as a result of continued contact of the soil and an excess of the carbonate up to the 2 weeks interval in the case of the Dunkirk clay. The preliminary treatment of the Volusia silt loam seemed sufficiently intense, however, to satisfy its tendency to absorb lime within the time of experimental conditions.

The marked effect produced by the acids generated by oxidation of formaldehyde or sugar is very plainly demonstrated by the large decrease of $CaCO_3$ in the formaldehyde checks.

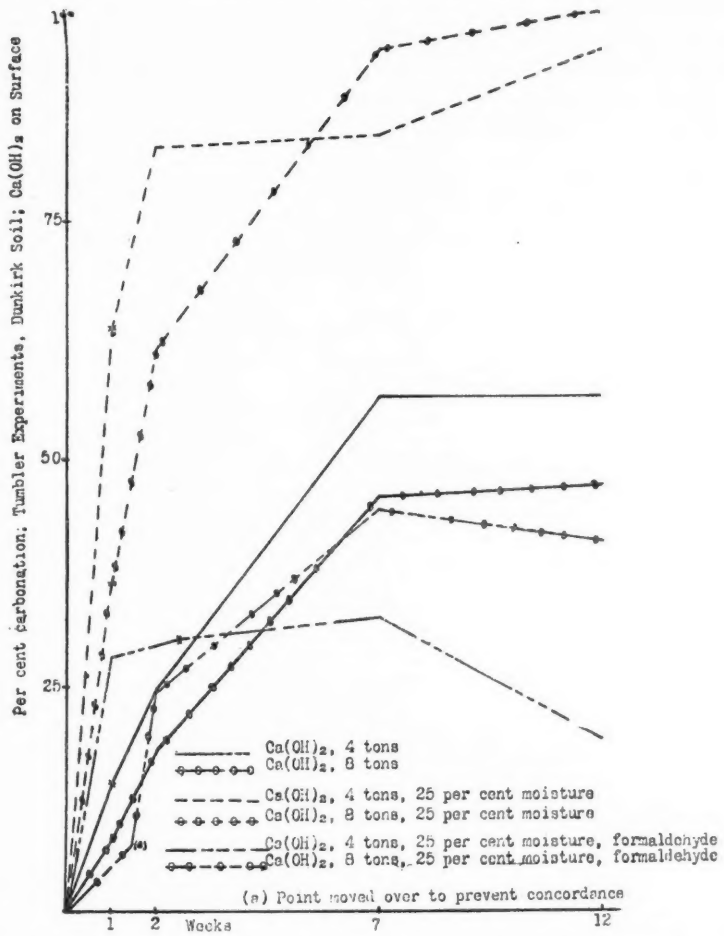

FIG. 9. TUMBLER EXPOSURE EXPERIMENTS, DUNKIRK SOIL—$Ca(OH)_2$ ON SOIL SURFACE (TABLES 40, 41 AND 42)

Supplementary tumbler experiments with calcareous Dunkirk soil; studies as to the source of the CO_2*, which combines with the* $Ca(OH)_2$ *lying upon the soil surface*

In the foregoing tumbler exposure experiments there was established no definite demarkation between the amount of CO_2 derived from atmospheric diffusion and that engendered biologically within the soil. Furthermore, in the maintenance of a definite moisture content, the surface applications of calcium hydrate were subjected to wetting. A supplementary set of Dun-

TABLE 43

Comparisons of $CaCO_3$ *contents of alkaline air-dry soils, used in tumblers as the basis of treatments supplemented by 4 and 8-tons* CaO *equivalent check treatments of* $CaCO_3$ *and the same soils subsequent to further moist contact; 25 per cent moisture content being maintained by additions of distilled water and also 20 per cent formaldehyde*

PERIOD OF CONTACT	AIR-DRY		MOISTURE 25 PER CENT DISTILLED H_2O		MOISTURE 25 PER CENT FORMALDEHYDE	
	4 tons	8 tons	4 tons	8 tons	4 tons	8 tons
			Dunkirk clay loam*			
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Initial	1.55	3.04				
2 weeks			1.40	2.80	1.21	2.69
12 weeks			1.40	2.82	0.81	2.19
			Volusia silt loam			
Initial	1.65	3.21				
4 weeks			1.64	3.20	1.37	3.00
14 weeks			1.64	3.21	1.27	2.65

* Dunkirk blank initially 0.41; after two weeks 0.155; and after 12 weeks 0.025 per cent carbonate, with formaldehyde treatments.

TABLE 44

Carbonation in supplementary set of Dunkirk clay loam; $Ca(OH)_2$ *exposed on surface to atmospheric diffusion and to soil-atmosphere* CO_2 *as compared to exposure to soil-atmosphere* CO_2 *alone; water and 20 per cent formaldehyde used for maintenance of moisture constant supplied by capillarity*

PERIOD OF EXPOSURE	MOISTURE CONTENT 25 PER CENT MAINTAINED BY ADDITIONS OF CO_2-FREE DISTILLED H_2O				MOISTURE CONTENT 25 PER CENT MAINTAINED BY ADDITIONS OF 20 PER CENT FORMALDEHYDE			
	CaO 4 tons exposed	CaO 4 tons closed	CaO 8 tons exposed	CaO 8 tons closed	CaO 4 tons exposed	CaO 4 tons closed	CaO 8 tons exposed	CaO 8 tons closed
	Per cent carbonation	Per cent carbonation	Per cent carbonation	Per cent carbonation	Per cent carbonation	Per cent carbonation	Per cent carbonation	Per cent carbonation
weeks								
2	62.6	19.8	64.7	11.8	46.1	10.4	47.4	6.7
7	76.6	24.7	79.0	14.1	70.5	25.0	59.7	14.1

kirk soil was, therefore, introduced in order to differentiate in part between the two sources of CO_2 and also to eliminate the necessity of wetting the surface charges of lime.

In the bottoms of a number of tumbler containers $\frac{1}{2}$ inch of clean sand was placed. Upon this was placed a uniformly compacted $3\frac{1}{2}$-inch depth of soil. Through the center of the soil and to the bottom of the glass extended the beveled edge neck of a 9-cm. funnel. This funnel was used as a means of introducing water and formaldehyde into the sand at the bottom of the

tumblers and thus, by capillarity, to insure the maintenance of moisture content. Upon the surface of the soils in the tumblers was placed a layer of sand $\frac{1}{4}$ inch in thickness. Upon this were spread charges of $Ca(OH)_2$ at the rates of 4 and 8 tons per acre surface. In this way direct contact between treatment and moist soil was prevented. One series, comprising one-half of the tumblers, was left exposed. The remaining tumblers were completely covered with black paper which was then made air-tight by means of vaseline-paraffin mixture. The containers are shown in figure 10. Excepting the probable meagre amount of air which would diffuse down the small neck of the funnel and up into the soil, the charges would in one case be subjected to only the biologically evolved CO_2. On the other hand, the surface applications, devoid of the impervious paper covering, were probably more extensively bathed by air movements than were the paper-covered surface treat-

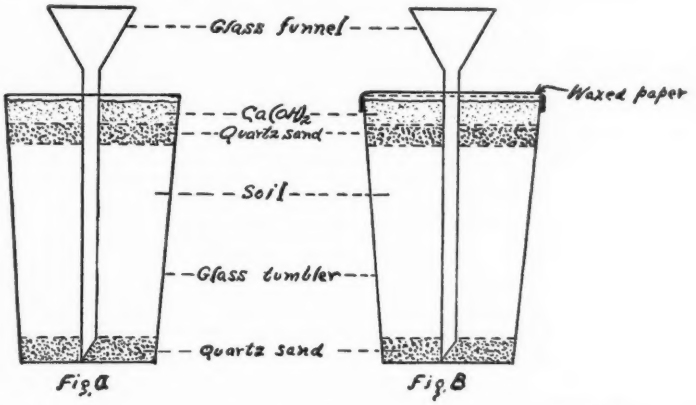

FIG. 10. EQUIPMENT USED IN COMPARING SURFACE CARBONATION WITH RESTRICTED AND UNRESTRICTED DIFFUSION

ments, because of greater opportunity afforded for diffusion between soil air and the atmosphere, and also because of the greater lateral movement of atmosphere across the surface.

The data from this exposure experiment are contained in table 44. These results show some diffusion of CO_2 from the alkaline moist soil to the overlying layer of lime, where no external exposure was permitted. The larger part of the gain in CO_2 comes, however, from the atmosphere. In the case of the formaldehyde tumblers, the carbonation effected was much greater than in the former cases. In this set the capillary rise of any acid produced was stopped by the layer of sand intervening between soil and $Ca(OH)_2$. The partial neutralization of acetic acid by $Ca(OH)_2$ was thus prevented. The tumblers were proved by culture plate tests to be sterile from the effects of formaldehyde. Therefore, no CO_2 could be evolved biologically. However, the action of

oxidized acids upon the initial $CaCO_3$ of the calcareous soil would furnish some CO_2 and effect carbonation of the adjacent surface hydrate. Additional CO_2 may have been derived through oxidative processes inherent to the soil and by a giving up of CO_2 condensed upon the surfaces of the soil particles.

The data indicate that hydrated lime lying upon the surface of a moist soil will, in reverting to carbonate, derive most of its absorbed CO_2 from the lateral movement of air across the surface, rather than from the outward diffusion of soil atmosphere.

This phase of the problem was further studied in the field under conditions simulating those of practice.

FURTHER STUDIES CONCERNING THE SOURCE OF THE CO_2 WHICH COMBINES WITH THE $Ca(OH)_2$ LYING UPON THE SOIL SURFACE

As previously stated, the foregoing data, obtained in the supplementary tumbler experiments, were secured with a soil which had been rendered alkaline by subjection to preliminary treatment with precipitated $CaCO_3$. This preliminary treatment and the method of control were such as to establish conditions which would be considerably at variance with those that would be encountered in the field. The problem was, therefore, attacked from another angle.

In applying lime in the field, it is quite probable that applications are most generally made upon either a dry dust or soil mulch secured by cultivation, or upon a natural compact soil mulch. In either case the lime applied would be in contact with a comparatively dry soil, toward which it would be relatively inactive. It is therefore probable that most of the finely divided hydrate applied to a soil surface would all be converted to the carbonate form before its incorporation with the soil, unless the working-in were done very shortly after the application. For, it has been shown that reasonable applications of lime are very quickly converted to the carbonate when mixed with the soil, and that surface applications are still more rapidly converted. Disregarding rainfall and dew, this surface-lying lime has but two sources from which it may obtain the CO_2 required for its carbonation, namely, diffused soil atmosphere and aerial movements across the soil surface.

With the above points in mind, surface applications of lime were exposed in the following manner. Mason jar covers were used as containers for the exposed charges of lime. A layer of glass wool was first laid upon the bottom of the container. Upon this was placed a definite amount of dry sifted sawdust with which had been mixed 0.3 gm. of $Ca(OH)_2$. One-half of the number of jar covers used were perforated before the introduction of the lime charges in the sawdust mixture: the others were unchanged. The layer of glass wool intervening between the lime and the surface of the moist soil was intended to simulate the inactive surface mulch to be expected under field

conditions. The perforated and unperforated containers were then simultaneously placed side by side over the surfaces of four soils. Protection against rainfall was afforded without restriction of lateral movement of air. After 7 days of exposure the jar-top containers were placed in desiccators and conveyed to the laboratory for carbonate determinations. The experiment was then repeated with four other soils during a subsequent period of the same number of days. The data secured from these exposures are given in table 45.

TABLE 45

Effect of diffusion of soil atmosphere from field cylinders, in accelerating the carbonation of surface applications of lime, where direct contact of lime and soil was prevented; exposure for 7 days, August, 1918

SOIL		TREATMENTS JUNE, 1913; 5 YEARS PRIOR TO PRESENT EXPERIMENT	CARBONATION		
Type	Condition		Perforated bottoms permitting upward diffusion of soil atmosphere	Unperforated bottoms preventing upward diffusion of soil atmosphere	Increase induced by movement of soil atmosphere through perforations
			per cent	*per cent*	*per cent*
Cookeville fine sandy loam	Optimum	None	70.54	52.94	17.60
Crossville fine sandy loam	Optimum	None	80.93	59.50	21.43
Gallatin brown loam	Optimum	None	75.82	62.70	13.12
Jackson sandy loam	Optimum	None	79.33	69.73	9.60
Cumberland loam	Moist	Manure, 48 tons	45.61	25.59	20.02
Cumberland loam	Moist	Manure, 48 tons; Limestone, 16 tons	52.34	32.31	20.03
Cumberland loam	Moist	Hydrated lime, 8 tons	46.26	23.54	22.72
Cumberland loam	Moist	Limestone, 16 tons	49.90	27.57	22.33
Average			62.59	44.23	18.36

Discussion of data of table 45

In the case of each of the eight soils, there occurred a greater carbonation where the perforations permitted an upward diffusion of the soil atmosphere as supplementary to that of aerial movements across the surface of the charges of $Ca(OH)_2$ lying upon the top of the soil. The carbonation effected in the eight charges having access to the diffused soil atmosphere resulted in an average of 62.59 per cent of the absolute, while the eight charges not subject to the diffused CO_2 gave an average of 44.23 per cent of the possible. This increase, attributable to the diffusion through the perforations, amounted to an average of 18.36 per cent of the theoretical carbonation, or 41.3 per cent of the carbonation effected in the unperforated-container exposures. These data are consistent and support those of table 44. Nevertheless, they do not con-

clusively demonstrate that the greater carbonation induced by proximity to the soil atmosphere is of necessity attributable to CO_2 diffused from the soil. It might be assumed that there occurred a diffusion of both CO_2 and moisture from the soil to the surface charges contained in the perforated tops. On the other hand, it might be assumed that only moisture vapor passed from the soil and to the surface charges of lime, through the perforations in the covers. For, under the latter conditions, the $Ca(OH)_2$ would have reverted to the carbonate more rapidly in the perforated covers than in the unperforated ones, where no supplementary moisture was available to accelerate conversion of the exposed hydrate from solid to solution phase. In other words, were the adjacent perforated and unperforated tops bathed by aerial atmosphere and by it alone, the more moist $Ca(OH)_2$ would effect a more rapid extraction of CO_2 from the air passing over the surfaces. This deduction follows from the preliminary laboratory studies in which it was shown that it is essential to have sufficient moisture to maintain the solution of the hydrate in case the carbonate reaction is to proceed without hindrance. In the field, under humid conditions and with minimum wind velocity, the moisture, chemically liberated in the hydrate-to-carbonate reaction, might remain sufficiently long to aid in the maintaining of the solution phase of the hydrate. However, under average conditions, the atmosphere, unsaturated with reference to moisture, would rapidly conduct the chemically liberated H_2O away from the surface of the liberating hydrate. Hence, it is obvious that acceleration of the carbonate reaction induced by the adjacency of the hydrate to the soil atmosphere might possibly be attributable to the activating influence of diffused moisture, even to the exclusion of CO_2 of soil atmosphere derivation.

In order to clarify this point, the procedure which yielded the data of table 45 was slightly modified and amplified, in such a way as to afford an abundance of CO_2-free moisture to surface charges of $Ca(OH)_2$, at the same time protecting these from direct diffusion of soil atmosphere. In addition to the exposures in perforated and unperforated containers, a third series of containers was simultaneously and adjacently exposed. This supplementary series was made from pairs of jar tops, two nested covers being used for each charge exposed. The inner and upper top was perforated, while the outer and lower one was unperforated. The latter contained a definite amount of asbestos, which was moistened with CO_2-free water. The space between the outer and inner containers was filled with melted parafin, so that no moisture could escape from the reservoir except through the perforations in the bottom of the inner and upper container, the latter containing $Ca(OH)_2$. The hydrate in this experiment was mixed with asbestos instead of dry sawdust as in the former experiment. Charges of 0.5 gm. were used instead of 0.3 gm. as formerly. Three conditions were thus maintained in this exposure experiment. Intimate mixtures of lime and asbestos were exposed at the soil surface: (a) without direct access to CO_2 of the soil atmosphere, or to

TABLE 46

Relative effects of moisture vapor and CO_2 of diffused soil atmosphere from field cylinders in accelerating the carbonation of surface applications of hydrated lime, where direct contact of lime and soil was prevented

SOIL	WEATHER CONDITIONS	SEASON OF EXPOSURE	NUMBER OF DAYS OF EXPOSURE	TREATMENT JUNE, 1913—5 YEARS PRIOR TO PRESENT EXPERIMENT	CARBONATION		
					Unperforated bottoms preventing upward diffusion of moisture vapor and CO_2	Perforated bottoms permitting upward movement of moisture from moist asbestos	Perforated bottoms permitting upward diffusion of both moisture vapor and CO_2 from soil
					per cent	*per cent*	*per cent*
Cumberland loam	Rainy	October	7	Manure, 48 tons	78.90	87.93	92.04
Cumberland loam	Rainy	October	7	None	82.45	84.70	86.96
Jackson sandy loam	Rainy	October	7	None	62.44	73.49	74.46
Cumberland loam	Fair	November	4	Manure, 48 tons	53.56	60.99	66.31
Cumberland loam	Fair	November	4	None	47.04	51.40	76.80
Cherokee sandy loam	Fair	November	4	None	53.02	58.50	79.48
Jackson sandy loam	Fair	November	4	None	55.44	58.66	75.12
Average					61.84	67.95	78.74

supplementary moisture, except that of the aerial atmosphere; (b) without direct access to CO_2 of the soil atmosphere, but with access to supplementary moisture as furnished by the asbestos reservoir; (c) with direct access to both CO_2 and moisture of the soil atmosphere. The exposures were sheltered without restriction of lateral air movement. The results are incorporated in table 46.

The data of table 46 show that, in the case of each of the seven soils used, the same relationship is maintained in the respective speeds of the carbonate reaction, as induced by the three conditions of exposure. The unperforated containers gave an average carbonation of 61.84 per cent of the possible; the containers with perforations permitting movement of moisture from the asbestos reservoir gave 67.95 per cent of that possible, as an average; while the containers with perforated bottoms permitting access of both CO_2 and moisture from the soil gave an average percentage of 78.74. It is thus evident that the soil-derived moisture was instrumental in accelerating the carbonate reaction. If it is assumed that as much moisture passed through the perforations above the asbestos as passed from the soil through similar perforations, or if the moisture diffused from the asbestos was sufficient to give maximum speed of carbonation with the atmospheric CO_2 available, then it follows that the hydrate derived from the soil atmosphere the lesser part of the CO_2 with which it combined. This conclusion is further fortified by the exposures which gave the data of table 47.

Supplementary exposures demonstrating that CO_2 of the soil atmosphere is in part responsible for the carbonation of $Ca(OH)_2$ lying on the surface of a soil mulch

In studying further the source of the CO_2 which effects the carbonation of soil surface applications of $Ca(OH)_2$ the perforated jar top nests of table 46 were again used. In one set of these nested containers the outer and lower receptacle contained a definite amount of CO_2-free asbestos which rested upon a thin bed of glass wool; while the upper and inner jar cover contained a definite amount of $Ca(OH)_2$ mixed with the asbestos, the mixture resting upon a thin layer of glass wool as in the case of the lower and outer jar of the nest. In another set a definite amount of $Ca(OH)_2$ was mixed with the asbestos of both the upper and lower jar covers. In this way the upward diffusion of the CO_2 of the soil atmosphere was unimpeded in one case, while in the other the lower mixture of $Ca(OH)_2$ and asbestos served as a trap protecting the upper charge of $Ca(OH)_2$. The exposures of the surface charges of lime with and without the underlying trap layers were made during mild winter days of December and January at the Tennessee Station farm. The results from the two series of exposures are given in table 47.

The data incorporated in this table show that the surface charges of $Ca(OH)_2$ which were underlaid by the $Ca(OH)_2$ filters, were less extensively

carbonated than were those underlaid with asbestos only. Thus the lower layer effected an estoppage of CO_2 diffusion from the soil atmosphere to the surface-lying charges of $Ca(OH)_2$. The asbestos-lime filter layer showed a considerable increase in its CO_2 content subsequent to exposure. In fact, the average increase in the filter layer represented an amount greater than the average differential between the protected and unprotected surface layers. This may be due in part to the two-fold surface exposure offered by the two

TABLE 47

Movement of CO_2 from the soil atmosphere to surface-lying charges of $Ca(OH)_2$ as indicated by the trapping of CO_2 by means of a $Ca(OH)_2$- asbestos-mixture filter intervening between the soil surface and an overlying exposed charge of $Ca(OH)_2$ mixed with asbestos; perforated-bottom metal containers; soil quite moist

SOIL	DATE OF EXPOSURE	$Ca(OH)_2$ CHARGE	CO_2 GAIN IN $Ca(OH)_2$ FILTER	CARBONATION	
				Surface charge with blank asbestos filter	Surface charge with $Ca(OH)_2$ asbestos filter
		gm.	*per cent*	*per cent*	*per cent*
Cumberland loam	December 19–23	0.6		79.44	78.04
Cherokee sandy loam	December 19–23	0.6		69.05	63.43
Jackson fine sandy loam	December 19–23	0.6		50.27	48.57
Cherokee sandy loam	January 30–February 3	2.0	10.95	69.04	67.16
Cumberland loam	January 30–February 3	2.0	11.87	52.25	50.39
Jackson fine sandy loam	January 30–February 3	2.0	10.64	53.27	52.38
Cumberland loam	January 30–February 3	2.0	16.00	53.40	51.06
Average			12.37	60.96	58.72

separate $Ca(OH)_2$ layers, the filter layer being 2 gm. in each case, and it might be assumed that not all of the surface downward movement of CO_2 was taken care of by the upper layer. Had the exposures been made during the summer, the actual amount diffused to the surface would doubtless have been more extensive.

Taken in connection with the preceding tables, the data of table 47 may be considered as proving definitely that a movement of soil atmosphere to surface-lying $Ca(OH)_2$ is only in part responsible for the conversion of the hydrate to the carbonate.

FURTHER STUDIES AS TO THE SPEED OF THE CARBONATE REACTION, IN THE CASE OF THE SURFACE EXPOSURES OF $Ca(OH)_2$, AS COMPARED TO THAT OBTAINED WHEN THE HYDRATE IS WITHIN THE SOIL MASS

The data obtained from the analyses of the upper and lower strata of the soil of the lysimeter tanks showed no appreciable difference in the occurrence of carbonates in the two strata, at the end of one year of exposure, where applications were made at the rate of 8 tons of CaO per 2,000,000 pounds of soil. Almost, if not, complete carbonation of the lime incorporated with the soil was effected in both strata. While these analyses demonstrated but little difference in the ultimate $CaCO_3$ content of the respective layers at the end of the initial annual period, they do not establish the relative speeds of carbonation in the two strata. However, the differential was determined in each instance of the tanks receiving CaO at the rates of 32 and 100 tons. These heavier treatments showed incomplete carbonation and a consistently greater $CaCO_3$ content in the upper stratum. Furthermore, in the tumbler-exposure experiments a consistently greater carbonation was effected in the surface applications, as compared with the carbonation effected from equal amounts mixed throughout the soil mass, under both dry and moist conditions.

Because of the greater atmospheric CO_2 content of a normal soil, as compared with that of the atmosphere above its surface, this would not be expected; unless it is assumed that the unrestricted movement of the aerial atmosphere would tend to offset the greater percentage CO_2 of the more restricted soil atmosphere. The continued occurrence of hydrated lime in the 32 and 100-ton treatments suggested several possibilities. It seemed possible that complete carbonation might be retarded by the protective action of $CaCO_3$ coatings around the numerous minute lime particles, even in the presence of an abundance of atmospheric CO_2. However, such a pseudo equilibrium would be frequently disrupted by rainfall as is evidenced by the continued leaching of hydrate from these heavily limed tanks and also by the almost complete carbonation attained in the wetted surface soils in the tumbler experiments. The moisture content of the tanks receiving the heavy lime treatments is usually low, because of quick evaporation after light rains and rapid drainage, followed by rapid evaporation, after heavy rains. This would tend to favor such a condition of restricted carbonation because of a diminished CO_2 generation. However, the atmospheric CO_2 determinations of table 36 demonstrated the poverty of CO_2 in the soil atmosphere of the heavily limed tanks. This marked decrease of atmospheric CO_2 strongly indicated a diminution of biological activities, to be attributed to the partial sterilization effected and maintained by the lime. There remained, however, the possibility that the less restricted movement of the surface atmosphere would bring to the surface applications greater amounts of CO_2 than would be diffused by the soil atmosphere to the lime incorporated within the soil. In order to elucidate this point it seemed advisable to submit hydrated lime to the surface

and soil atmospheres, without permitting actual contact between lime and soil. This was done in two ways. At first, 0.5-gm. charges of water-slaked and oven-dried lime were weighed on uniformly folded 9-cm. filters and enclosed in flat wire frames. Four of these were then placed upon a fallow soil surface and four were imbedded in the soil at a depth of $2\frac{1}{2}$ to 3 inches. Protection from rain was afforded without effecting any restriction in wind movement. After different periods the charges were analyzed for CO_2. This procedure was later discontinued because the filters incorporated within the soil became apparently more moist than those of the surface. Possibly the factor of greater moisture supply thus afforded to convert the hydrate from solid to liquid phase was offset by the tendency toward diminution of pore space and restricted CO_2 movement through the paper placed within the soil. The paper cartons were replaced by glass cartridges $\frac{1}{2}$ inch by $3\frac{1}{2}$ inches. One end of each cartridge was closed by a brass wire gauze and $\frac{1}{4}$ inch of quartz sand was then inserted. Enough sand to fill the cartridges to within $\frac{1}{4}$ inch was then mixed uniformly with 0.5 gm. $Ca(OH)_2$ and introduced into the glass tube. A layer of sand $\frac{1}{4}$ inch thick was next added and the end of the cartridge closed by means of a wired wire-gauze cap. These cartridges were placed upon the surface and in the soil simultaneously and subsequently analyzed for $CaCO_3$ as formerly. This procedure gave the results recorded in table 48.

The data of table 48 show that without exception the lime placed within the soil underwent carbonation more rapidly than did that exposed on the surface. In this experiment no chemical alteration was effected within the soil and no biologically accelerated or depressed CO_2 evolutions were involved. Apparently, then, if no appreciable absorption of lime by soil were to transpire and the lime incorporated within the soil were in amounts sufficiently small to activate, rather than depress biological agencies, the results would have been the reverse of those obtained in the tank and tumbler exposure experiments. This point will be further considered.

The contents of table 48 also bring out a very interesting comparison between the rapidities of carbonation which were effected in the several soils. The organic-matter content of the sandy loam and that of the stony loam were very low. The volatile matter determined on 1-mm.-mesh material from these two soils was 2.1 per cent and 2.0 per cent, respectively, as compared to 5.6 per cent from the Dunkirk silt loam. The sandy soils were of fossil delta derivation and were almost entirely devoid of clay or silt. The sandy loam is that of the quadrangle of the New York State College of Agriculture, while the stony sandy loam is located just east of Caldwell Hall. Only about one-third of the stony loam was sufficiently fine to pass the 1-mm. sieve. This soil had also been recently top-dressed with an indefinite amount of manure. The silt loam is that of the plats of Caldwell Field on the University Farm. While the total organic matter in the sands was decidedly less than in the case of silt, the freedom of diffusion of the CO_2 of the sand

TABLE 48

Comparison of the speed of carbonation of $Ca(OH)_2$ on surface and that within fallow soils, where direct contact of lime and soil was prevented by mixing lime with sand and placing the mixture in glass tubes

SOIL	LOCATION OF EXPOSED LIME	DATE OF EXPOSURE	PERIOD OF EXPOSURE	CHARGE EXPOSED	CARBONATION IN SEPARATE SIMULTANEOUS EXPOSURES						
					A	B	C	D	E	F	Average
			days	*gm.*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Dunkirk silt loam	On surface	July 7	8	0.5	10.6	11.8	10.7	10.4	10.4	9.9	10.6
	In soil	July 7	8	0.5	20.7	21.1	17.8	18.3	18.3	18.9	19.2
Dunkirk silt loam	On surface	July 15	17	0.5	16.3	15.9	18.6	16.3	13.5	13.1	15.6
	In soil	July 15	17	0.5	32.7	33.3	38.6	38.8	39.9	31.4	35.8
Dunkirk stony sandy loam	On surface	May 31	4	0.5	7.3	5.9	6.5	6.5			6.6
	In soil	May 31	4	0.5	24.3	20.6	33.1	32.6			27.7
Dunkirk stony sandy loam	On surface	June 23	8	0.5	13.7	11.3	10.9	10.6			11.6
	In soil	June 23	8	0.5	45.1	40.5	46.5	45.8			44.5
Dunkirk sandy loam	On surface	May 2	2	0.5	46.5	46.5	49.6	42.7	41.5	48.8	45.9
	In soil	May 2	2	0.5	59.9	67.1	66.8	58.1	53.9	55.3	60.2
	On surface	May 24	2	0.5	49.5	48.5	48.2				48.7
	In soil	May 24	2	0.5	61.8	55.8	57.0	65.7			60.3

was probably greater because of larger pore space and less colloidal material to exert the phenomenon of surface adsorption of the gas.

The results of table 48 were verified by repetition with slight variation of technic, at the University of Tennessee Station Farm, during the months of August and September. In this case the glass tubes which contained the hydrate charges had an inside diameter of $\frac{13}{16}$ inch, and were $3\frac{1}{4}$ inches long. The charges of lime were mixed with asbestos or sawdust and placed in the tubes, the ends of which were closed with glass wool. The tubes which were placed in the soil were about 3 inches below the surface. The differences in the extent of carbonation resulting from the two conditions of exposure are shown in table 49. These data also indicate very forcibly that, under the seasonal conditions encountered, reasonable amounts of lime would carbonate more rapidly within the soil at a depth of about 3 inches, than upon the surface, were it not for a depression of biological activities induced by contact of lime and soil and isolation of the lime from aerial CO_2.

It thus seems probable that when amounts of lime sufficient in quantity to satisfy a soil's coefficient of absorption, and also afford carbonate residues sufficient to justify analytical work, are mixed with the soil, the following may be anticipated. A part of the lime is absorbed in neutralizing the soil's acid properties; a part is neutralized by the CO_2 of the free soil water, together with that of the atmosphere and possibly that condensed in the soil film. The remainder, if any, has a tendency, at least temporarily, to restrict or depress the further generation of CO_2 within the soil, until the excess of the lime within the soil is further, in part or in whole, converted to the carbonate. With the restricted tendency toward CO_2 generation, the excess of lime in the soil would then carbonate less rapidly than would that lying on the surface, since the latter would have more freedom of contact with the surface movement of the CO_2 of the aerial atmosphere. With regard to light applications of lime such as those most generally to be met with in practice, the following would seem to be what would be reasonably expected. The conversion to carbonate of an application immediately mixed with the soil and one left on the surface would both be very rapid and of so nearly equivalent speed as to be considered identical for all practical purposes. However, an application that would be considered as a light one on the basis of an acre 6, an acre 8, or an acre 12 inches would be proportionally heavier when stirred in with only the upper surface inch, or the surface of 2 inches. The dryness of the mulch, augmented by the presence of fine uncarbonated lime, would most probably reduce to a minimum any CO_2 generations in the mixture of lime with the upper surface. Then, if the diffusion of CO_2 from the moist underlying soil is the same to both the mulched lime and that lying on the surface, we would expect a more rapid carbonation of that left undisturbed on the surface. For, the data of table 10 show that an admixture of lime with a dry mulch exerts a protective influence and that lime so mixed reverts to the carbonate less rapidly than when left exposed.

TABLE 49

Additional comparisons as to speed of the carbonation of $Ca(OH)_2$, *when mixed with asbestos or sawdust in glass tubes and placed within and upon the surface of fallow soils, where direct contact of lime and soil was prevented;* weight of lime charge, 0.3 gm.*

SOIL	TREATMENTS APPLIED 5 YEARS PREVIOUS TO PRESENT EXPERIMENT	DATE OF EXPOSURE	CONTAINING TUBE STOPPERED WITH	CARBONATION	
				In soil	On soil surface
				per cent	*per cent*
Cookville fine sandy loam	None	August 29 to September 5	Glass wool	68.63	41.75
Crossville fine sandy loam	None	August 29 to September 5	Glass wool	54.22	31.83
Gallatin brown loam	None	September 21 to September 28	Glass wool	44.78	17.24
Jackson sandy loam	None	September 21 to September 28	Glass wool	27.19	23.03
Cumberland loam	8 tons CaO as $Ca(OH)_2$	August 15 to August 19	Cotton	33.27	19.19
Cumberland loam	16 tons of limestone	August 15 to August 19	Cotton	36.79	18.55
Cumberland loam	48 tons of manure	August 20 to August 26	Glass wool	48.31	25.14
Cumberland loam	Limestone, 16 tons; manure, 48 tons	August 20 to August 26	Glass wool	45.62	28.34
Average				44.85	25.63

* All soils well supplied with moisture.

However, there is one additional point to be considered with reference to the speed of the carbonate reaction, as it occurs in the soil, as compared to that on the surface, when the direct contact factor is eliminated. As in the case of the charges of tables 45 and 46 where access to the soil atmosphere was afforded through the perforations in the containers, thus preventing physical contact and preventing partial sterilization, the question of the differences in the moisture supply within the soil and on its surface is germane. Therefore, it seemed advisable to expose the glass-tube charges on the surface and in the soil under conditions which would insure availabe moisture to both exposures. Therefore, the following procedure was followed. Six-tenth gram charges of $Ca(OH)_2$ were mixed with dry asbestos, or sawdust, and placed in glass tubes $\frac{13}{16}$ inch in diameter and $3\frac{1}{4}$ inches long as recorded in table 49. Instead of being stoppered with glass wool as formerly, both ends of the

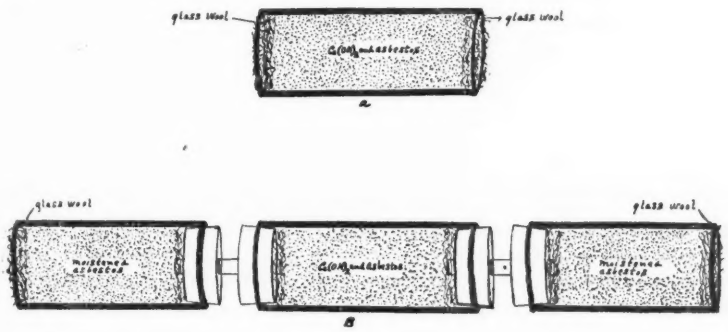

FIG. 11

a, $Ca(OH)_2$ containers used in securing data of Tables 48, 49, 51, 52 and 53.

b, Modified containers for supplying moisture to both surface and intra-soil charges of $Ca(OH)_2$, used in securing data of table 50.

tubes were closed with 1-hole stoppers. Through these was inserted a short $\frac{1}{4}$-inch glass tube, the other end of which was inserted in a 1-hole stopper and this stopper fitted into another glass tube of the same diameter as the one containing the lime. This second tube contained a porous mixture of asbestos and sawdust, which when saturated with distilled water afforded free movement of moisture and air from the atmosphere into the lime chamber. The tubes are illustrated by the sketch, figure 11, B. Working with three well moistened soils, the data of table 50 were obtained.

These data show that during fall weather the soil atmosphere will effect initially a more rapid conversion of the hydrate to the carbonate than will be effected in the case of surface exposures, where an abundance of moisture is made available to the surface charges, as well as to the charges exposed in containers within the soil. One element to be considered in this respect is that of season. Were heavy charges of hydrate exposed and extensive CO_2

fixation thus provided for, it would seem that a local paucity of atmospheric CO_2 might result and unless CO_2 diffusion to the deceminated areas should transpire, the disparity would later probably be diminished, if not reverted. These factors will be considered in succeeding paragraphs.

TABLE 50

Supplementary exposures of $Ca(OH)_2$ *in fallow soils and upon the surfaces of the same soils where moisture vapor was furnished both exposures; direct contact of lime and soil prevented by glass tube containers; weight of lime charges, 0.6 gm.*

SOIL	CONDITION OF SOIL	DATE OF EXPOSURE	CONTAINER TUBES STOPPERED WITH	CARBONATION	
				In soil	On surface
				per cent	*per cent*
Cherokee sandy loam	Wet	October 17–24	Glass wool	11.70	8.92
Cumberland loam	Wet	October 17–24	Glass wool	11.37	8.47
	Wet	October 17–24	Glass wool	10.82	8.47
Average				11.30	8.62

The factors of season and size of charges in influencing the speed of the carbonate reaction with surface and intra-soil exposures of $Ca(OH)_2$

The question as to influence of the magnitude of charge seemed essential. The additional factor of season also seemed germane, the previous exposures having been made only during warm periods. Accordingly, charges of 2 gm. of high-grade $Ca(OH)_2$ were mixed with asbestos, placed in glass cylinders and exposed on the surface and within two soils during mild winter weather experienced during the latter part of December at the Tennessee Station Farm. The procedure was then repeated, charges of 2.5 gm. of $Ca(OH)_2$ being used with five other soils. The results are given in table 51. These data show a considerable increase above the amount of absolute carbonation recorded in the case of the lesser charges of table 49, and at the same time show a reversal in the extent of the carbonation of surface exposures of $Ca(OH)_2$, as compared to those charges placed within the soil. The greater surface exposure offered by the increased charge of hydrate; more restricted CO_2 generation, because of the lower soil temperature; and decreased diffusions of soil atmosphere as a result of increased free soil water, appear as factors tending to decrease the extent of carbonation within the soil as compared to that effected in the case of the surface charges.

Additional exposures were later made. In these a simultaneous parallel between 0.6-gm. and 3-gm. charges of $Ca(OH)_2$ was secured for each of five soils, during April, at the Tennessee Station Farm. The spring season was unusually late and the soils were rather moist. The data obtained from these exposures are given in table 52. Again in every instance the surface carbonation was greater than that induced within the soil. When calculated to a

uniform basis, the results show in each instance, a greater actual carbonate formation effected by the 3-gm. charges as compared with the 0.6-gm. charges. The increases, however, are far from being proportionate. As a matter of fact, such a proportionate increase could hardly be expected, for although the amounts of hydrate mixed with the asbestos are in the proportion of 1 to 5, the area of access of soil atmosphere to hydrate is the same for each lime-container tube. On the other hand, the smaller charges may have reached a pseudo-equilibrium because of carbonate layer formations, thus minimizing

TABLE 51

Variations in the speed of the carbonate reaction obtained when excessive charges of $Ca(OH)_2$ *were exposed simultaneously on the surface and within the soil during the winter; glass containers, lime-asbestos mixtures, glass wool stoppers and no contact between soil and lime*

SOIL	DATE OF EXPOSURE	CONDITION OF SOIL	$Ca(OH)_2$ CHARGE	CARBONATION	
				Soil surface exposure	Intra-soil exposure
			gm.	*per cent*	*per cent*
Cumberland loam*	December 19–23	Wet	2.0	20.96	18.25
Cumberland loam	December 19–23	Wet	2.0	21.88	18.81
Jackson fine sandy loam	December 30–January 2	Rather wet	2.5	11.65	10.09
Cherokee sandy loam	December 30–January 2	Rather wet	2.5	11.72	11.51
Cumberland loam*	December 30–January 2	Rather wet	2.5	13.61	11.90
Cumberland loam	December 30–January 2	Rather wet	2.5	12.33	11.74
Cumberland loam	December 30–January 2	Rather wet	2.5	12.13	11.96
Average				14.89	13.47

* Each sample of Cumberland loam from a different cylinder and 5 years previously subjected to different treatments.

the effective surface and actually permitting CO_2 to be diffused through the tube without further carbonation having been effected; while the larger charge of further active surface may have absorbed this CO_2 which possibly may have diffused unabsorbed through the smaller charges.

The parallel between the 0.6-gm. and 3-gm. charges was again observed by making additional exposures after the same soil had warmed up considerably during the latter part of May. The data secured in this exposure are given in table 53. These data are in every instance the reverse in relationship to those of tables 51 and 52, but in harmony with those of tables 48, 49 and

50. While the intra-soil exposures again show a more extensive carbonation within the soil than on its surface, for both the 0.6-gm. and the 3-gm. charges, the extent of carbonation in the heavier charges is again not proportionate to the increase in amounts exposed. The relationship between the variation in amount of charges and the uniformity of exposure to soil atmosphere has been considered in the preceding paragraph.

TABLE 52

Variations in the speed of the carbonate reaction obtained with light and heavy charges of $Ca(OH)_2$ *under simultaneous surface and intra-soil exposures, during early spring; glass containers; ignited soil and lime mixtures, glass wool stoppers and no contact between soil and lime*

SOIL	DATE OF EXPOSURE	CONDITION OF SOIL	$Ca(OH)_2$ CHARGE	CARBONATION			
				Of theoretical		On uniform basis of 0.6 gm.	
				Soil surface	In soil	Soil surface	In soil
			gm.	*per cent*	*per cent*	*per cent*	*per cent*
Cherokee sandy loam	April 2–8	Moist	0.60	30.41	24.93	30.41	24.93
	April 2–8	Moist	3.00	7.42	6.81	37.10	34.05
Cumberland loam	April 2–8	Moist	0.60	31.53	25.90	31.53	25.90
	April 2–8	Moist	3.00	11.15	8.30	55.75	41.50
Jackson fine sandy loam	April 2–8	Moist	0.60	32.50	20.20	32.50	20.20
	April 2–8	Moist	3.00	11.44	4.99	57.20	24.95
Cumberland loam * (a)	April 2–8	Moist	0.60	30.18	27.61	30.18	27.61
	April 2–8	Moist	3.00	11.07	7.81	55.35	39.05
Cumberland loam † (b)	April 2–8	Moist	0.60	32.98	28.73	32.98	28.73
	April 2–8	Moist	3.00	10.54	7.58	52.70	37.90
Average				20.92	16.29	41.57	30.48

* Received 16 tons of dolomite and 48 tons of manure 6 years prior to present experiment.
† Received 16 tons of dolomite 6 years prior to present experiment.

From the survey of the data of tables 48 to 53, it appears that more extensive carbonation is effected within the soil when seasonal conditions are such as to accelerate CO_2 generation and diffusion to the extent that the restricted soil atmosphere diffusions overcome the factor of less restricted movement of the aerial atmosphere with its lesser CO_2 content. With lower soil temperatures and depressed diffusion incident to increase in free water content, the surface exposures of hydrate demonstrate a more rapid carbonation.

TABLE 53

Variations in the speed of the carbonate reaction obtained with light and heavy charges of $Ca(OH)_2$ *under simultaneous surface and intra-soil exposures, during late spring and early summer; glass containers, quartz and asbestos mixture with lime; glass wool stoppers and no contact between soil and lime.*

SOIL	DATE OF EXPOSURE	CONDITION OF SOIL	$Ca(OH)_2$ CHARGE	CARBONATION			
				Of theoretical		On uniform basis of 0.6 gm.	
				Soil surface	In soil	Soil surface	In soil
			gm.	*per cent*	*per cent*	*per cent*	*per cent*
Cherokee sandy loam	May 19 to June 4	Optimum	0.6	32.42	68.21	32.42	68.21
	May 19 to June 4	Optimum	3.0				
Jackson fine sandy loam	May 19 to June 4	Optimum	0.6	30.81	90.09	30.81	90.09
	May 19 to June 4	Optimum	3.0	10.82	18.21	54.10	91.05
Cumberland loam*	May 19 to June 4	Optimum	0.6	31.61	85.10	31.61	85.10
	May 19 to June 4	Optimum	3.0	20.81	26.28	104.05	131.40
Cumberland loam†	May 19 to June 4	Optimum	0.6	58.24	64.51	58.24	64.51
	May 19 to June 4	Optimum	3.0	19.27	21.94	96.35	109.70
Average				29.14	53.48	58.22	91.44

* Received 30 tons of manure 6 years previous to present experiment.

† Received 16 tons of dolomite and 48 tons of manure 6 years previous to present experiment.

DOES BURNT LIME DERIVE CO_2 FOR ITS CARBONATION BY CHEMICAL ACTION UPON SOIL ORGANIC MATTER?

The statement that caustic lime "burns up the humus" of a soil is commonly heard in agricultural discussion and is to be found in many writings. The belief is prevalent that a deleterious action upon soil organic matter follows the use of caustic lime, while no such result is to be attributed to the use of ground limestone. Two viewpoints are maintained, relative to the action of lime on soil organic matter. By one group it is held that the action of lime, in the assumed depletion of organic matter, is primarily a chemical function. The following citations are typical. Richardson (56) believes, "Its destructive action is due to its caustic character. It rapidly destroys humus, and thus tends to rob the soil of its most valuable constituent." Reinecke (55) writes, "The very fact, however, that they are alkaline and hence caustic makes their extensive use dangerous since caustic lime (lime in oxide and hydrate form) destroys soil humus." It might well be noted at this point that shippers of hydrated lime experience no difficulty, when using paper bags as containers for the water slaked product. Hopkins (36) teaches

that precautions should attend its use for, "in other words the use of lime, if continued tends rapidly to exhaust the soil and ultimately to leave it practically ruined." It is interesting to note in this connection that such an observation was made following the use of marl, in 1856, by Kitchell (40), who noted almost complete sterility for a period of 18 years following the use of excessive amounts of marl. The sterility, however, disappeared upon the use of barnyard manure. To quote, "On the property of Mr. James H. Struble in Sandiston Township, is a barren spot of land to which marl, or calcareous sinter, was applied 18 years ago. Since this time, as I was informed, no vegetables would grow except when a heavy coat of barnyard manure or vegetable matter is applied to it and then but one luxuriant crop can be obtained." The character of the soil was not specified. It is possible that such an observation may be accounted for by the use of the toxic marls to be found in that locality. Dr. Hopkins (36) also cites Webster as defining *caustic* as being "capable of destroying the texture of anything or eating away its substance by chemical action." He then states, "This definition well describes the action of caustic lime upon the organic matter of the soil." It might here be stressed that the inherent and characteristic activity of caustic or burnt lime is due to its affinity for *water*. This affinity is readily satisfied by moisture available from adjacent soil and aerial atmosphere, when burnt or unslaked lime is lying upon the soil surface. Subsequent to the taking up of moisture and conversion of the oxide to the hydrate, neither the solid phase of this later nor the solution phase of hydroxide appears to exert any destructive action on soil organic matter. This may be deduced from the data derived from experiments involving contact of both dry and moist soil with the solid hydrate (table 54), and the continued contact of the concentrated hydroxide solution with the several soils as given in table 55.

Christie and Martin (10) studied the effect of a 0.4 per cent application of CaO on an alkaline soil, by examining the concentration of the soil extract 24 hours after incorporation of the lime. They found a marked increase in the amount of calcium, magnesium, potassium and phosphorus, with a decrease in nitrates. In discussing their results they state, "It is a well known fact that lime decomposes organic matter in soils and, therefore, it might well be contended that the increases in total solids were due to soluble organic matter. In case of about half of the soils examined, the electrical conductivity of the soil extract was measured. The figures obtained were in direct relation to the total-solids determination, showing that at least the greater part of the increases were due to inorganic and not to organic matter."

By another group, it is contended that any decrease in soil organic matter, following the use of burnt or hydrated lime, is attributable to the acceleration of biological activities; and hence that the judicious use of lime is no more to be discriminated against than is soil cultivation, or fertilizer stimulation, both of which also effectuate the same result. The more conservative view, that there is lacking proof to support the contention that burnt lime effects

chemical destruction of soil organic matter under conditions of field practice is held by Frear (22), Wheeler (70, 71) and Fippin (17). While numerous experiments could be cited to demonstrate the accepted truth as to acceleration of biological activities following the use of lime, no differential studies have been put forward to demonstrate separately the action to be attributed to chemical and biological factors.

The data most generally utilized in an attempt to substantiate the claim that CaO will, by chemical action, deplete the soil organic matter are those reported by Frear (20) in 1900. In this work, which was done 18 years after the inauguration of the experiment, the limed plats toward the west end of the tiers are compared with a composite of all the check plats, some of which are at least one-tenth mile distant. The comparisons were made and the conclusions were drawn on the assumption that initially the plats were of identical or very comparable composition. Dr. Frear has since showed that there exists a marked dissimilarity in the present composition of different portions of the driveways between the tiers. These driveways have been continuously in grass, since the inauguration of the experiment. The limed plats were analyzed 12 years later by the writer (47). In this case, however, the basis of comparison was a composite of the four check plats immediately adjacent to the plats receiving lime alone and between these and the plats treated with ground limestone. These analyses emphasize one comparison as pertinent. In 1899, Hess found by furnace combustion of 0.5-mm. composite samples of the five quadruplicate series of untreated plats 2.830 per cent organic matter as compared to 2.530 per cent from a composite of the four burnt lime plats. On the other hand in 1912 the writer analyzed 100-mesh composites of the four untreated plats immediately adjacent to the four plats receiving burnt lime alone, sampled simultaneously in the same manner. These later analyses give 2.555 per cent organic matter for the untreated soil as compared to 2.529 per cent for the burnt lime plats. Comparing the samplings of the four limed plats as obtained by Hess and again by MacIntire, 12 years later, it appears that the burnt lime plats have lost but 0.001 per cent of organic matter. On the other hand if the composite of the four untreated plats immediately adjacent to the lime plats is considered as comparable to the composite of all untreated plats, as sampled by Hess, then the *untreated plats have lost 0.275 per cent of organic matter*. It is certainly as consistent to compare the average composition of all the check plats at one period, with the average composition of the four check plats adjacent to the lime plats at another period, as it is to compare the average composition of all the check plats with the average composition of the four limed plats at corresponding periods.

On the assumption of uniform original composition, now established by Dr. Frear as untenable, a slightly less organic matter content, 0.026 per cent, is found in the CaO-treated soil than is to be found in the limestone-treated plats. The difference is small, however, and is well within the error of careful

sampling and analysis, as may be seen from the compositions of the eight burnt-lime-treated plats (table 9). Eliminating from consideration the question of error of sampling, there remains the additional undetermined factors, namely, variation in influence upon biological activities and *differences in the amounts of root stubble incorporated in the two series of lime-treated plats.* More recently, however, Dr. Frear has discussed the matter comprehensively in the light of the more recent data. From a comparison between the data of Hess and the above-cited analysis by the writer, Dr. Frear (22) justifies his conclusion that data from the general fertilizer plats of the Pennsylvania Station do not warrant the statement that organic matter has been destroyed by chemical action of the quick lime. He further stated that his original data had been utilized commercially as the basis of a limestone propaganda to an extent further than he felt was justified.

There remains an additional undetermined factor, i.e., the possibility of difference in the incipient action of lime upon the original soil organic matter and that exerted upon the residues from the initial organic matter and the organic matter incorporated from stubble since the end of the 18-year period.

In addition to the data reported by the Pennsylvania Station analyses obtained from plats which had been limed for a period of ten years have been reported by Bear (3) of the West Virginia Station. In this case the soil was sampled at the beginning of the experiments, and the question of variation due to sampling also was considered. Bear concluded that the application of burnt lime is more conducive to the destruction of soil organic matter than is limestone.

In carefully checked plat work, Mooers (53) has concluded from determinations of ammonia-soluble matter that the use of 1800 pounds of burnt lime per acre has slightly decreased the more active humus as compared to the untreated plats. In experiments with imbedded pots, Wheeler, Sargent and Hartwell (72) also have reached the same conclusions. It is interesting to note, however, that phosphates and other fertilizers devoid of destructive characteristics effectuated the same result. This is a strong indication that acceleration of biological activities may account for the decrease in active organic matter. Other contributions on the subject are those of Hartwell and Kellog (29), Ritter (57), Andre (2) and Densh (11). The latter writer obtained evidence of ammonia formation from contact between lime and peat, vegetable mould, etc., after an 82-day period of contact. No such duration of uncarbonated lime could occur, however, under normal field conditions. It is, of course, conceded that nitrogen may be split off as NH_3 from organic forms, by hydrolytic processes induced by $Ca(OH)_2$. However, if the lime is mixed in the soil, the soil's absorption power would inhibit loss of NH_3 as gas. This was demonstrated in the case of the experiment embodied in table 54, in which instance no NH_3 could be aspirated off. In combination with water this would certainly not be leached any more rapidly than would nitrates, the production of which lime and other favorable agencies

are known to accelerate. Furthermore, admitting the doubtful hypothesis that complete carbonation would not transpire prior to harrowing in of applied lime, any NH_3 set free chemically within the soil would quickly undergo change to ammonium carbonate or urea and probably nitrification as a result of stimulated biological activities. But, marked increase in ammonification, as a result of partial sterilization, has been shown by Russell and Hutchinson (59) to be probably the primary cause of increased fertility attendant upon the sterilizing treatment. In light of the above facts, any chemical ammonification induced by burnt lime within the soil assumes the rôle of an argument for, rather than against, its use.

It is often stated, with possible justification, that *simultaneous* surface applications of manure and burnt lime should not be made, because of the loss of ammonia or ammonium carbonate by volatilization. There would appear to be no particular reason why such applications should be made simultaneously. Granting that lime will accelerate loss of ammonia, when lime and manure are applied to the surface at the same, or approximately the same time, it should be remembered that we have no experimental evidence upon which to base the assumption and also that ammonia losses from manure freshly applied to the surface in the field are also to be sensed *in the absence of lime.*

The chemical destruction of organic matter by lime would involve the liberation of CO_2 which would be partly or completely absorbed by the $Ca(OH)_2$, thus hastening its conversion to $CaCO_3$. Hopkins (36) states, "The lime breaks down the organic compounds and unites with the liberated carbon dioxide or other acid products," and "Caustic lime is not only a powerful agent in hastening the destruction of organic matter . . . . " Again, "Thus there are two principal effects produced by applying lime to soils: one . . . . and the other is a more active decomposition or destruction of the soil itself, especially of its organic matter or humus content." It is, then, of interest and of importance to determine whether the applied lime derives CO_2 required for carbonation partly from chemical action of lime on organic matter, as well as from atmosphere, soil atmosphere and accelerated biological activities. An attempt was made to obtain data on this phase of the question.

The following plan was adopted: Fifty-gram charges each of two calcareous soils, the brown loam and the grey silt loam of the mulch exposure tests of table 10 previously described, were weighed into 300-cc. Erlenmeyer flasks. These were provided with two-hole rubber stoppers, through which were inserted cotton-plugged glass tubing with Geissler stop-cocks attached. Each treatment and check was made in triplicate. To each flask was added a 0.4-gm. charge of high-grade $Ca(OH)_2$. The two soils used were from basket experiments and two years previously had received treatments of precipitated $CaCO_3$ equivalent to 9000 pounds of CaO in excess of the "lime requirement" indicated by the Veitch method. In this instance

absorption of the applied hydrate was minimized and most, if not all, of the charge of caustic lime left free to exert any possible chemical activities upon organic matter. The condition to which the triplicate charges of each soil were submitted were dry, both sterile and non-sterile, and wet, both sterile and non-sterile. The dry soil was sterilized in an autoclave by subjection to 15 pounds of steam pressure for 30 minutes. Soil, hydrated lime, and distilled water for soil moisture were sterilized separately and mixtures made of the sterile substances. It should not be assumed that powdered hydrated lime is absolutely sterile, *per se*. At the request of the writer, Dr. J. K. Wilson, of Cornell University, made several plate cultures from bottled samples of the freshly slaked, dry, hydrated lime used by the writer in the tumbler-exposure experiments and he obtained a vigorous growth of fungi.

TABLE 54

Analyses made to determine amounts of any CO_2 liberated as a result of contact of 0.4 gm. $Ca(OH)_2$ and 50 gm. of soil in closed flasks under dry and moist conditions, both sterile and non-sterile; time, 126 days

SOIL	TREATMENT	CO_2 IN SOIL AND ATMOSPHERE OF FLASKS	CO_2 IN BLANKS	CO_2 LIBERATED CHEMICALLY OR BIOLOGICALLY FROM ACTION OF LIME ON SOIL	
				Gm. from 50 gm. of soil	Per cent
		gm.	*gm.*		
Cumberland loam	CaO dry and sterile	0.0622	0.0546	0.0076	0.015
	CaO dry and non-sterile	0.0706	0.0614	0.0092	0.018
	CaO wet and sterile	0.0681	0.0731	0.0050	0.010
	CaO wet and non-sterile	0.0976	0.0989	0.0013	0.003
Silty loam	CaO dry and sterile	0.0203	0.0211	0.0008	0.002
	CaO dry and non-sterile	0.0256	0.0249	0.0007	0.001
	CaO wet and sterile	0.0410	0.0372	0.0038	0.007
	CaO wet and non-sterile	0.0592	0.0501	0.0091	0.018

Subsequent to admixtures of dry soil and $Ca(OH)_2$, 7.5 cc. of water was added to each of the 50-gm. charges which were to be kept moist. After mixing, the flasks were freed of their atmospheric CO_2, closed and kept in a darkened closet without further disturbance. At the end of 48 days single determinations of CO_2 from checks and each triplicated treatment were made as a guide for future analytical work. No activity of lime having been noted, the remaining duplicate flasks were left for a total period of 126 days. At the end of this period the flasks were aspirated to absolutely insure the absence of gaseous CO_2. Possible presence of free NH_3 also was considered and the aspirated air tested therefor, with negative results. If any ammonia was liberated by the treatment, it remained absorbed by the soil. Carbonate determinations were then made on the 50-gm. charges of soil. The averages

of duplicate determinations are given in table 54. These analyses show that no positive chemical decomposition ensued as a result of long continued contact of soil and lime. While an appreciable increase in $CaCO_3$ might be expected to occur from fixation by the lime of any CO_2 liberated through enhanced biological evolution, it appears from the data that the charge of lime was sufficiently large to insure enough of $Ca(OH)_2$ in solution to effect partial or complete sterilization. These conditions were much more severe and were extended over a much longer period than would ever be encountered in practice. No field conditions would ever effect such long continued contact between undissolved $Ca(OH)_2$ and moist soil. For, as has been shown, carbonation is relatively rapid in near-surface applications in reasonable quantities. Neither would there occur in practice such extensive admixture of soil and treatment; nor would there obtain such extensive surface contact of soil and dissociated hydrate during the period prior to its carbonation under practical conditions.

If no positive decomposition of organic matter is effected chemically by lime under the conditions maintained in this experiment, it is difficult to assume that lime under field conditions would accomplish such a result.

Effects produced by contact of saturated $Ca(OH)_2$ *solution and soil*

The question was still further considered by subjecting the soil to possibly even more severe treatment. Quadruplicate samples of a number of soils were weighed into 300-cc. Erlenmeyer flasks which were then stoppered with cotton and sterilized by overnight heating at 105°C. in an electric oven. Two of the charges were then freed from the CO_2 of their atmosphere and agitated in closed flasks for 3- and 4- and 15-hour periods, with 50 cc. of saturated lime-water containing 0.0596 gm. of CaO, or 0.238 per cent, 0.298 per cent and 0.596 per cent, respectively, for the 25-, 20- and 10-gm. soil charges. These amounts would be equivalent to 4760 pounds, 5960 pounds and 11,920 pounds, respectively, of CaO per acre 2,000,000 pounds of soil. The two remaining charges were treated in the same manner, except that CO_2-free distilled water was substituted for the lime-water. After vigorous and continued agitation for the specified periods the carbonate CO_2 was determined by liberation through additions of 20 cc. of 1 to 1 HCl. The results are given in table 55.

Inspection of these data shows that, within laboratory error, attendant upon very careful manipulation, no difference was obtained between the treatments of distilled water and lime-water. With four of the ten soils, negative results were obtained. Two gave indications of increase less than 0.0025 per cent; three gave apparent increase less than 0.0175 per cent, while one alkaline muck gave 0.0270 more CO_2 for the lime-water. The high percentage of organic matter in the muck soils would certainly appear to afford conditions calculated to permit any destructive action by the lime-water, especially when the latter was present at the rate of over 11,000 pounds of

TABLE 55

Nugatory action resulting from agitated contact of sterile soils and saturated water solution of $Ca(OH)_2$ in closed flasks—possible decomposition of organic matter anticipated and allowed for by absorption of liberated CO_2 in $Ca(OH)_2$ with subsequent determinations of combined CO_2 as compared with parallel blanks of CO_2-free distilled water

SOIL	REACTION TO LITMUS	VOLATILE MATTER	CHARGE	TREATMENT	PERIOD OF AGITATED CONTACT	CO_2 FOUND		CO_2 LIBERATED FROM SOIL BY CONTACT WITH $Ca(OH)_2$	
		per cent	*gm.*		*hours*	*gm.*	*per cent*	*gm. per charge*	*per cent*
Volusia silt loam	Acid	10.7	25	$Ca(OH)_2$	3	0.0069	0.0276	0.0006	0.0023
	Acid	10.7	25	H_2O	3	0.0063	0.0253		
Dunkirk clay loam	Alkaline	5.2	25	$Ca(OH)_2$	15	0.0441	0.1764	0	0
	Alkaline	5.2	25	H_2O	15	0.0442	0.1768		
Fine sandy humus loam	Neutral	12.1	25	$Ca(OH)_2$	4	0.0286	0.1144	0.0027	0.0108
	Neutral	12.1	25	H_2O	4	0.0259	0.1036		
Volusia silt loam	Acid	7.8	25	$Ca(OH)_2$	3	0.0055	0.0220	0	0
	Acid	7.8	25	H_2O	3	0.0055	0.0220		
Volusia fine sandy loam	Acid	15.3	25	$Ca(OH)_2$	4	0.0154	0.0615	0.0031	0.0123
	Acid	15.3	25	H_2O	4	0.0123	0.0493		
Genessee silt	Alkaline	12.2	25	$Ca(OH)_2$	3	0.0110	0.0440	0	0
	Alkaline	12.2	25	H_2O	3	0.0110	0.0440		
Virgin Genessee silt	Alkaline	14.3	25	$Ca(OH)_2$	3	0.0125	0.0500	0.0002	0.0008
	Alkaline	14.3	25	H_2O	3	0.0123	0.0492		
Muck	Alkaline	67.0	20	$Ca(OH)_2$	3	0.0924	0.4620	0	0
	Alkaline	67.0	20	H_2O	3	0.0924	0.4620		
Muck	Acid	94.8	10	$Ca(OH)_2$	3	0.0059	0.0590	0.0017	0.0170
	Acid	94.8	10	H_2O	3	0.0042	0.0420		
Muck	Alkaline	67.8	10	$Ca(OH)_2$	3	0.0489	0.4890	0.0027	0.0270
	Alkaline	67.8	10	H_2O	3	0.0462	0.4620		
Average									0.0070

CaO per acre under such exaggerated conditions of contact. The results, however, could not be considered as absolutely proving the decomposition of organic matter by hydrated lime, even if the several minute plus differences were taken as positive indication of chemical activities. For, it is quite possible that some substances of acid character might be precipitated by the lime, thus affording substances more easily decomposed by the acid used to liberate combined CO_2. Then, too, in the mineral soils some potassium exchange would be expected to insure, and this strongly dissociated base might effect, slight decomposition of organic matter.

It is apparent that under the sterile intensified experimental conditions there is exhibited no loss of organic carbon from the action of hydrated lime. It is, therefore, difficult to believe that there occurs in the field any *chemical decomposition* of carbonaceous material as a result of contact between soil and caustic lime.

Field cylinder studies relative to the comparative activities of CaO, $Ca(OH)_2$ *and finely divided* $CaCO_3$ *upon initial and supplementary soil organic matter*

The question of the chemical decomposition of soil organic matter, either that of initial stores or that applied was, in tables 54 and 55, considered solely as the basis of the relationship of such a possible decomposition to the generation of CO_2 which would influence the speed of the reversion of hydrate to carbonate. However, the exposed cylinder experiments used in the carbonation studies afforded an opportunity for the determination of any difference in the residual organic matter subsequent to the use of burnt lime as compared to that residual from chemically equivalent carbonate checks. No brief is offered for burnt or hydrated lime as compared to ground limestone, nor is consideration given to the comparative virtues or commercial values as related to their use in practice. The object sought was to ascertain whether it is true that burnt or hydrated lime effects *chemical disintegration* and decrease of soil organic matter. As previously pointed out, the hydrate and oxide applications may be considered as identical, since there was an abundance of moisture in the soil at the time of incorporation, and this moisture quickly effected a hydration of the oxide. It should be stressed that the experimental conditions imposed in the cylinder studies were much more severe than would be those encountered in agricultural practice. The lime treatments of the cylinder experiments were mixed throughout the upper 6 inches of the 8 inches of soil placed in each cylinder. Thus the added CaO and $Ca(OH)_2$ had extensive contact with the soil before reversion to carbonate could take place. On the other hand, it has been shown that quick carbonation ensues when lime is left exposed on the soil surface, and hence in practice a large part, it not practically all, of the applied lime will be incorporated with the soil as the carbonate, rather than as the hydrate, provided the lime is spread in fine condition.

It is obvious that even with ground limestone of unusual fineness there would be a considerable disparity between the surface exposure of such particles and that of particles of carbonate formed from applied oxide and hydrate. Such a differential in surface exposure would mean a variation in the alkalinity of the soil medium as induced by difference in amounts of lime dissolved by the soil solution and absorbed by the soil. Therefore, pure precipitated carbonate devoid of hydrate, rather than limestone was used as a control. The soil used was thoroughly mixed, screened, and remixed, and it was assumed that each 200-pound lot of soil placed in each 1/10,000-acre cylinder was of the same composition initially. Accordingly, after the speed of carbonation studies had indicated complete carbonation of the applied lime, samples were taken for the determination of total residual organic matter. The determinations were made by the wet combustion method as modified by Schollenberger (61). The absorption of carbonate CO_2 liberated by acid, and that engendered by the oxidation process was accomplished by means of NaOH contained in elongated absorption towers. These were filled with alternating pockets of solid glass rods and glass beads. The absorption solution was washed from the towers into 500-cc. graduated flasks. Barium chloride was added and the solutions made to mark and agitated. After the $BaCO_3$ had settled, 200-cc. aliquots of the clear supernatant hydrate were titrated, phenolphthalein being used as an indicator.

Discussion of the results of tables 56 and 57

In considering the results of tables 56 and 57 it should be remembered that, disregarding the flask-container studies of tables 54 and 55, any variation in the residual organic matter of these field cylinders might be attributed to combined chemical action and biological activation induced by the treatment, or solely to either agency, according to the viewpoint assumed. But, the data of tables 54 and 55 demonstrate that there occurs no positive disintegration of organic matter involving the liberation of CO_2. However, it is possible that some organic matter may be so changed as to render it more susceptible to oxidation by biological activities or by an enhancement of the inherent oxidative properties of the soil. In considering the activities of CaO and $Ca(OH)_2$, it is only the immediate effect with which we are concerned, that is, the effect produced up to the time of complete conversion of hydrate to carbonate. For, after the conversion of the hydrate to the carbonate, it is then a question of the activation induced by finely divided $CaCO_3$. Hence, a comparison between the amount of soil organic matter remaining at the end of a long period subsequent to treatments of CaO or $Ca(OH)_2$ and that residual after a treatment of ground limestone would be analogous to a comparison between the effect of pulverulent $CaCO_3$ and coarser ground limestone.

As has been pointed out, the analytical results offered by Frear and those obtained by the writer in studies of the Pennsylvania Station plats are to be

considered in the light of the fact that we have no accurate knowledge as to the amounts of plant residues turned under in either the limestone or the burnt lime plats. But in the case of the cylinder experiments there was no interference from varying crop residues, and such incorporations of organic

TABLE 56

Total organic matter residual in Cumberland loam soil of field cylinders subsequent to incorporation of separate applications of CaO, $Ca(OH)_2$ *and* $CaCO_3$, *on the basis of chemical equivalence to 4,000 pounds of* CaO *per 2,000,000 pounds of soil; with and without supplementary applications of manure*

LABORATORY NUMBER	RIM NUMBER	SERIES	DATE OF SAMPLING 1913	TREATMENT		CARBONATE CO_2	TOTAL CO_2	ORGANIC CO_2 MOISTURE-FREE BASIS	AVERAGES		
				Lime	Manure per acre				Number of cylinders sampled	Number of analyses	Organic CO_2
					tons	*per cent*	*per cent*	*per cent*			*per cent*
2692	1	M	July 28	CaO	None	0.00	5.22	5.22	2	5	5.28
2697	1	L	August 11	CaO	None	0.01	5.34	5.33			
2693	2	L	August 11	$Ca(OH)_2$	None	0.02	4.96	4.94	2	5	5.02
2709	2	M	August 11	$Ca(OH)_2$	None	0.01	5.12	5.11			
2694	3	L	August 11	$CaCO_3$	None	0.02	4.94	4.92	2	4	5.07
2710	3	M	August 11	$CaCO_3$	None	0.01	5.23	5.22			
2711	7	M	August 11	CaO	12	0.00	5.55	5.55	2	4	5.57
2940	7	L	September 15	CaO	12	0.00	5.58	5.58			
2696	8	L	August 11	$Ca(OH)_2$	12	0.00	5.57	5.57	2	4	5.54
2960	8	M	September 15	$Ca(OH)_2$	12	0.00	5.51	5.51			
2922	9	L	August 15	$CaCO_3$	12	0.02	5.30	5.28	2	5	5.40
2931	9	M	August 15	$CaCO_3$	12	0.00	5.52	5.52			
2698	13	L	August 11	CaO	30	0.02	5.68	5.66	2	4	5.69
2714	13	M	August 11	CaO	30	0.00	5.71	5.71			
2699	14	L	August 11	$Ca(OH)_2$	30	0.02	5.78	5.76	2	5	5.67
2715	14	M	August 11	$Ca(OH)_2$	30	0.00	5.68	5.68			
2925	15	L	August 15	$CaCO_3$	30	0.02	5.61	5.59	2	4	5.58
2934	15	M	August 15	$CaCO_3$	30	0.02	5.58	5.56			

matter as were made were of uniform character and of definite extent. The assurance of the necessary uniformity of initial composition was much more nearly approached in the cylinder experiments than is possible in the case of the Pennsylvania plats. For, in the latter case, the usual interpretation

which has been placed upon the chemical results from those plats is based upon the assumption of initial uniformity of composition in the area embraced by the plats. *That area is 18 acres in extent.* Even were it not for the results of Frear, which have demonstrated such an hypothesis as erroneous, one conversant with the topography and soil-type variations of those plats would know such an assumption to be untenable. It remained to be determined whether the accuracy possible in the handling of cylinder experiments

TABLE 57

Total organic matter residual in Cumberland loam soil of field cylinders subsequent to incorporation of separate applications of CaO, $Ca(OH)_2$ *and* $CaCO_3$ *on the basis of chemical equivalence to 16,000 pounds of* CaO *per 2,000,000 pounds of soil; with and without supplementary applications of manure*

LABORATORY NUMBER	RIM NUMBER	SERIES	DATE OF SAMPLING 1913	TREATMENT		CARBONATE CO_2	TOTAL CO_2	ORGANIC MOISTURE-FREE BASIS	NUMBER OF CYLINDERS SAMPLED	NUMBER OF ANALYSES	ORGANIC CO_2
				Lime	Manure per acre						
					tons	*per cent*	*per cent*	*per cent*			*per cent*
2704	25	L	August 11	CaO	None	0.43	5.36	4.93	2	4	4.98
2720	25	M	August 11	CaO	None	0.45	5.47	5.02			
2705	26	L	August 11	$Ca(OH)_2$	None	0.42	5.33	4.91	2	4	4.93
2721	26	M	August 11	$Ca(OH)_2$	None	0.44	5.38	4.94			
2706	27	L	August 11	$CaCO_3$	None	0.69	5.63	4.94	2	5	5.03
2691	27	M	July 28	$CaCO_3$	None	0.54	5.66	5.12			
2701	19	L	August 11	CaO	48	0.43	5.99	5.56	2	6	5.46
2717	19	M	August 11	CaO	48	0.41	5.77	5.36			
2702	20	L	August 11	$Ca(OH)_2$	48	0.47	6.07	5.60	2	4	5.57
2718	20	M	August 11	$Ca(OH)_2$	48	0.53	6.07	5.54			
2928	21	L	August 15	$CaCO_3$	48	0.67	6.23	5.56	2	7	5.63
2973	21	M	September 15	$CaCO_3$	48	0.54	6.24	5.70			

was of such extent as to register definitely any changes induced by the lime treatments or whether it was necessary to depend upon the smaller and more accurately controlled laboratory experiments.

The 2-ton-treatment results are given in table 56 while those derived from the 8-ton cylinders are embodied in table 57. The 2-ton treatment of CaO gave an average of 5.28 per cent organic CO_2, while the two $Ca(OH)_2$-treated cylinders gave an average of 5.02 per cent. These may be considered as being four identical treatments, giving an average of 5.15 per cent against

an average of 5.07 per cent for the two carbonate checks. The difference obtained by this comparison of averages is within the difference represented by the variations between maximum and minimum of the duplicates in each pair of treatments and checks. Again, the average of the four CaO and $Ca(OH)_2$ cylinders which received simultaneous application of manure at the rate of 12 tons per acre, amounted to 5.56 per cent organic CO_2, as against 5.40 per cent for the carbonate checks; while the four caustic treatments supplemented with manure at the rate of 30 tons per acre yielded an average of 5.68 per cent organic CO_2, as against 5.58 per cent for the carbonate and manure checks. These data might be construed as indicating a partial retardation of biological activities as the result of the incorporation of the 2-ton treatments of the caustic forms of lime, when compared to the activities resultant from the equivalent applications of carbonate. However, since the data of tables 11 to 16 show practically complete absorption of both oxide and hydrate, as well as carbonate, within 10 days after their incorporation, it would seem more reasonable to assume that the differences are within the limits of error induced by mixing, sampling and analysis. And furthermore, the data of tables 17 to 21 do not tend to support the viewpoint of depression induced by the oxide and hydrate, for in the cylinders yielding the data of these tables, the rate of application was four times that of the lighter applications on the 2-ton basis.

The average residual of initial organic CO_2 in the four 8-ton oxide and hydrate cylinders recorded in table 57 amounts to 4.96 per cent, this being a composite of an average of 4.98 per cent of CaO and an average of 4.93 per cent for $Ca(OH)_2$ treatments, as against 5.03 per cent for the $CaCO_3$ blanks, one of which contained 4.94 per cent, while the other gave a percentage of 5.12. Inspection of the results secured from the 8-ton treatments of burnt lime, hydrate and carbonate, each supplemented by manure, shows an organic CO_2 occurrence of 5.56, 5.60 and 5.56 per cent, respectively, in Series L, as against a respective content of 5.36, 5.54 and 5.70 per cent for the corresponding cylinders in Series M. The average of the results from the four CaO and $Ca(OH)_2$ cylinders of both series amounts to 5.52 per cent as against 5.63 per cent for the carbonate checks.

In a joint consideration of the data of the two tables, consistency demands that the greater difference obtained in the data derived from the 2-ton treatments of CaO and $Ca(OH)_2$ as compared to 2-ton-equivalent $CaCO_3$ treatments be viewed in the light of the reversal obtained in the comparison of the three forms when applied at the rate of 8-ton equivalence. Thus the plus differences of 0.08, 0.16 and 0.10 per cent, yielding an average plus difference of 0.11 per cent, accredited to the oxide and hydrate treatments as a summation of the 2-ton treatments from the no-manure, 12-ton-manure and 30-ton-manure cylinders, respectively, is opposed to the averages minus difference of 0.09 per cent obtained by averaging the minus differences of 0.07 and 0.11 per cent obtained from the 8-ton treatments in the no-manure and 48-ton-manure cylinders, respectively.

The data of tables 56 and 57 are certainly not out of harmony with those of tables 54 and 55, and together with them demonstrate that, in the case of the several soils studied, no chemical disintegration or destruction of organic matter results from such surface applications or incorporations of lime as would be expected in practice.

SUMMARY AND CONCLUSIONS

1. The development of the practice of liming and the need of more dependable data are pointed out.

2. A résumé is given of the available data relative to the reversion of burnt and hydrated lime to the carbonate in the atmosphere; while only opinions, instead of data, are available as to the carbonation ensuing subsequent to the application of lime to soils.

3. In preliminary chemical studies, without introducing the factor of the influence exerted by soils, it was demonstrated in tables 1 to 8, that:

a. Dry CaO and dry CO_2 do not react.

b. Dry $Ca(OH)_2$ and dry CO_2 do not react.

c. Blasting of high-grade lime, relatively free of silica, did not depress its hydrating or carbonating tendencies.

d. Eight 0.3-gm. charges of re-heated hydrated lime effected a more rapid reversion to the carbonate than did an equal number of charges of the original hydrate, when the sixteen charges were simultaneously exposed to normal humidity in outdoor October weather.

e. The same proved true with fourteen charges each of original and re-burnt hydrate exposed during the month of June, charges of from 0.3 gm. to 2.4 gm. having been used.

f. In June and July exposures of high-grade CaO and $Ca(OH)_2$ derived from slaking the same CaO, the CaO effected a more rapid reversion to carbonate in the case of the light charges; the reverse was true in the case of the heavy charges.

g. The film moisture from a dry glass container-tube was sufficient to initiate the carbonate reaction.

h. Complete hydration of CaO resulted from an overnight period of contact with moist air.

i. The formation of carbonate from $Ca(OH)_2$ is controlled by the amount of free water available to convert the $Ca(OH)_2$ from solid to solution phase.

j. The reversion of CaO to $CaCO_3$ must be preceded by the hydration and solution of the CaO; but when moist CO_2 is present, the reactions are so rapid as to be considered as simultaneous.

k. A protecting film-coating of $CaCO_3$, around included nuclei of $Ca(OH)_2$, is so effective as to retard further measurable carbonation in atmospheric exposure until the film surface is disrupted.

4. The question of the continuation of lime, as the hydrate, in soils was found to be a mooted one. As bearing on this point, the lime plats of the

Pennsylvania Station were analyzed and each of the eight plats was found to be free of uncarbonated lime (table 9).

5. In soil-surface carton-container exposures, without direct contact between soil mulch and underlying moist soil, applications of $Ca(OH)_2$ carbonated more rapidly on the surface of a dust mulch, than within the mulch. Equilibrium was attained before complete carbonation was effected. Grinding of the treatments in equilibrium was followed by further carbonation (table 10).

6. In a total of one hundred and twenty-eight 1/10,000 acre field-placed cylinders, a number were used for the purpose of studying the carbonate reactions in soils. Equivalent amounts of CaO and $Ca(OH)_2$ were used against precipitated $CaCO_3$ as a check over a period during which no leaching rains fell. In some instances manure also was included (pl. 1).

7. In the field cylinder studies, maximum carbonation of 2-ton CaO and $Ca(OH)_2$ applications ensued within 5 days after the admixture of the lime with the upper 6 inches of an 8-inch depth of surface soil; while complete absorption occurred within 10 days (tables 11 to 16, and fig. 2).

8. No difference could be observed between the activities of CaO and those of $Ca(OH)_2$ in the field cylinder soils (tables 11 to 21).

9. The addition of water, simulating rainfall, hastened both carbonation and subsequent absorption by the soil of applied CaO and $Ca(OH)_2$ (tables 11 to 17).

10. The carbonate reversion apparently reached its maximum before chance was afforded for its acceleration by CO_2 generated from supplementary treatments of 12, 30 and 48 tons of dry manure (tables 12 to 20).

11. Maximum carbonation of unabsorbed CaO, from both oxide and hydrate, occurred after contact extending over a period of between 19 and 38 days in the case of the 8-ton-per-acre treatments in the cylinders (tables 17 to 21).

12. The amounts of residual $CaCO_3$ derived from the unabsorbed portions of the applied CaO and $Ca(OH)_2$ were practically the same at the end of 38-, 47- and 61-day periods, in the case of the 8-ton treatments. Again supplementary manure treatments caused no determinable acceleration in the formation of $CaCO_3$ (tables 17 to 21).

13. Approximately 96 per cent of theoretical carbonation was attained from the unabsorbed residues of 8-ton chemically equivalent applications of CaO and $Ca(OH)_2$ which were made to a moist acid loam soil, precipitated $CaCO_3$ treatments having been utilized as checks (table 21).

14. The small differences in the amounts of $CaCO_3$ residual from applied CaO and $Ca(OH)_2$ as compared with the $CaCO_3$ checks might be accounted for by assuming a consistent analytical error, or the possible occlusion of $Ca(OH)_2$ nuclei. However, the abundance of soil moisture, especially in the cylinders receiving supplementary wettings, would minimize the latter possibility. These data and similar results from the lysimeters point to a slightly greater absorption from the more soluble hydrate during the period prior to its carbonation.

15. The analytical error to be expected in making CO_2 determinations upon moist soils was shown by periodic analyses of checks (table 22).

16. In an attempt to study the speed of the carbonate reaction involving only 2000 pounds per 2,000,000 pounds of soil, seventy impervious clay pots were used. The seven soils used in the pot studies were made alkaline by use of definite amounts of precipitated $CaCO_3$ and exposed, embedded, to the weather for more than a year before the applications of $Ca(OH)_2$. The simultaneous surface applications and mixtures with the upper 3 inches of the soils were sampled after 4- and 10-day periods. Considering the relative meagreness of the treatments, the results appear to justify the conclusion that both surface and intra-soil charges had attained maximum carbonation within 4 days (tables 23 and 24).

17. The carbonation of CaO in soils was further studied in field lysimeters which received only natural rainfall. Applications of 8, 32 and 100 tons were made and mixed throughout the entire 8 inches of soil. Precipitated $CaCO_3$, in chemically equivalent amounts, was used as a check. Both surface soil alone and surface soil underlaid by clay subsoil were considered in the studies (pl. 2).

18. In the lysimeter tanks over 60 per cent of theoretical carbonation occurred in the 8-ton treatments within 17 days, equilibrium having been attained between 218 and 366 days. In the 32-ton tanks, carbonation was gradual up to about 80 per cent of theory, at the end of the second year of exposure, little change having been observed in residual $CaCO_3$ between the end of the second and fourth annual periods. Something over one-half of the 100-ton treatments underwent reversion by the end of the second year of exposure. Little change was definitely recorded beyond that time (tables 25 to 30, and fig. 3).

19. Differential leachings, absorption and other factors recorded during the initial four years are considered in the discussion of the results from the lysimeters (table 31 and fig. 4).

20. The losses of total calcium salts from the several carbonate checks were very constant and independent of the extent of treatment; whereas the losses from the oxide tanks increased with increase in the amount of treatments (table 31 and fig. 4).

21. The leachings from all the oxide and carbonate treatments in the tanks without subsoil were very much richer in lime salts than those of the corresponding tanks which contained subsoil (table 31 and fig. 4).

22. At the end of the first, second, third and fourth years of exposure $CaCO_3$ occurrences were determined in the upper and lower strata, or halves, of the lysimeter soils. Practically equivalent amounts of $CaCO_3$ were found in the upper and lower strata of the 8-ton tanks. In the 32-ton and 100-ton tanks, the $CaCO_3$ contents of the several upper strata were uniformly and decidedly higher than those of the corresponding lower strata for each of the four annual periods, thus showing the influence of the adjacency of the several

upper strata to the movements of aerial atmosphere and also the interception of precipitated CO_2 (tables 32 to 35, and fig. 5).

23. Analyses of the soil atmospheres were made during the third and fourth years after placing. The results indicated a slight and continued depression in the CO_2 content of the 8-ton CaO tanks, suggesting either, or both, partial sterilization or effective alteration of the soil's tendency to condense CO_2 upon its surface (table 36).

24. The subsoil atmosphere withdrawals were much richer in CO_2 than were those obtained from the surface soil (table 36).

25. Tumbler containers were used in an indoor carbonation study of surface and intra-soil applications of $Ca(OH)_2$. Air-dry, moistened and formaldehyde-wetted soils, with and without sand mulches, were included in the experiment (pl. 3).

26. In the tumbler experiments, parallel surface and admixture exposures of 4 and 8 tons $Ca(OH)_2$ per acre surface, showed a much greater carbonation on the surface than within the soil mass, under both air-dry and moist conditions. The sand mulch registered a very decided retardation in the carbonate reaction, in the case of the Volusia silt loam (tables 37 and 38).

27. The comparison observed between the carbonation effected in the moist and in the dry Volusia series showed more extensive final carbonation in the dry series, thus indicating partial sterilization as having been induced in the moistened series. It further appeared that most, if not all, of the CO_2 which effected carbonation of the lime within the air-dry soil was available through infusion of aerial atmosphere into the soil and that the moistened soil experienced less of this aerial infusion (tables 37 and 38).

28. The carbonate reaction, if measured by accumulated $CaCO_3$, was practically inhibited within the Volusia soil treated with 20 per cent formaldehyde (table 39 and fig. 6).

29. In an attempt to maintain sterile conditions during exposure, through the use of 20 per cent formaldehyde, formic acid was produced as were also a sugar and para-formaldehyde, in considerable amounts; thereby were involved side reactions which nullified the apparent indications as to the absence of biological activities (Volusia and Dunkirk) (pl. 4).

30. Plate cultures demonstrated, however, that sterility was attained and maintained by the formaldehyde treatments.

31. In the tumbler experiments with both Dunkirk and Volusia soils the carbonation effected upon the surface was constantly greater than that which was brought about within the soil under air-dry condition and also when moisture was maintained by both water and 20 per cent formaldehyde additions. Again, in the case of the Dunkirk soil, as with the Volusia, the sand mulch effectively retarded carbonation (tables 37 to 42, and figs. 6, 7, 8 and 9).

32. As differing from the Volusia silt loam, the addition of water to the Dunkirk clay loam caused a more rapid and a greater ultimate carbonation

than was attained in the air-dry mixture from both surface applications and soil-mixed treatment. This held for both 4-ton and 8-ton treatments (tables 40 and 41, and figs. 8 and 9).

33. Initial and subsequent analyses of the calcareous check soils showed that the formaldehyde treatment reduced the carbonate initially present as residual from the preliminary $CaCO_3$ treatments (table 43).

34. In supplementary sets of Dunkirk clay loam, under restricted and unrestricted exposures, more than three-fourths of the CO_2 absorbed by the applied lime was derived from the aerial atmosphere, in the case of both 4-ton and 8-ton treatments (table 44 and fig. 10).

35. In simulating the conditions encountered when lime is applied upon the surface of a soil mulch, hydrated lime was exposed at the soil surface in circular containers, some having solid bottoms and some having perforated bottoms, the exposures being made at Knoxville during the month of August. Soil atmosphere diffused upward from the soil and through the perforations to the surface charges of $Ca(OH)_2$ and thus effected a more extensive carbonation than was obtained with the unperforated containers (table 45).

36. Additional exposures with modifications were made at Knoxville during October and November, in containers (as in 35). In this set, diffusions of (a) soil atmosphere and (b) moisture vapor from a saturated asbestos reservoir were permitted to surface-lying charges of $Ca(OH)_2$, as compared to adjacent hydrate which depended in the main upon aerial atmosphere for its supplies of both moisture and CO_2. It appeared that the greater carbonation brought about by upward diffusion of soil atmosphere (35) was in most part due to the moisture diffused and in lesser extent to the CO_2 derived from soil atmosphere diffusion, the greater part of the CO_2 fixation having been derived from aerial atmosphere (table 46).

37. Still further exposures were made at Knoxville during December and January. In this set, intervening trap charges of $Ca(OH)_2$ were placed between the moist soil surface and the overlying surface charges of $Ca(OH)_2$. The surface charges, which were protected by the intervening trap charges, were less extensively carbonated than were the ones devoid of traps and the trap charges showed an increase of CO_2, as a result of the interception of the soil atmosphere CO_2 which diffused to the surface. This again demonstrated that the CO_2 utilized in the carbonation of the surface applications of $Ca(OH)_2$ is in part due to the soil atmosphere but is derived in the main from that furnished by the aerial atmosphere (table 47).

38. Light charges of hydrated lime were mixed with quartz sand in glass cartridges and exposed within the soil at Ithaca during the months of May, June and July. With physical contact thus prevented, the lime charges within the soil underwent a much more rapid reversion to the carbonate than did the same mixtures in similar containers on the soil surface (table 48).

39. The exposures of (38) were repeated at Knoxville during August and September. The increase in CO_2 fixation in the embedded cartridges was

almost twice as great as that found in the cartridges which rested upon the soil surface (table 49).

40. The cartridge container exposures of $Ca(OH)_2$ were repeated during October at Knoxville with a slight modification. Moisture reservoir tubes attached to each end of each cartridge assured an abundance of moisture vapor to the contents of the surface charges, as well as to intra-soil charges. Greater CO_2 absorption again occurred within the soil (table 50 and fig. 11).

41. The surface and soil embedded exposures were again made during the month of December, at Knoxville, considerably larger charges of hydrate having been used. In this case the results were reversed, the soil surface exposures having been more extensively carbonated than were those which were placed within the soil (table 51).

42. Further simultaneous exposures on the surface and within the soil were then made at Knoxville during cool April weather, both 0.6-gm. and 3.0-gm. charges of hydrate having been placed within the cartridges. The surface charges were again more extensively carbonated in each instance than were those placed within the soil (table 52).

43. Still further exposures of 0.6-gm. and 3-gm. charges of hydrate, enclosed within glass cartridges, were made at Knoxville during May and June, after the soil had warmed up. In each instance it was found that more extensive carbonation had occurred where the charges were placed within the soil, the results being in accord with those obtained in making the summer exposures at Ithaca and late summer and fall exposures at Knoxville (table 53).

44. The open sandy types effected a more extensive carbonation than did the heavier types, though the latter were richer in organic matter (table 48).

45. The results reported by Hess, Frear and those of MacIntire from analyses of the Pennsylvania Station plats are considered in their interrelationship. From such a consideration it is pointed out that there has been secured no evidence which would indicate a chemical disintegration of soil organic matter as a result of the use of burnt lime.

46. In an effort to determine whether any of the CO_2 responsible for the formation of $CaCO_3$ was derived from chemical action of the applied $Ca(OH)_2$ upon soil organic matter, soil and heavy charges of $Ca(OH)_2$ were mixed and kept in closed containers for over 4 months under dry and moist conditions, both sterile and non-sterile (table 54).

47. No CO_2 evolutions, as indicative of chemical decomposition of soil organic matter, were obtained from these sealed contacts between 0.4-gm. charges of $Ca(OH)_2$ and 50-gm. charges of each of two soils during a contact period of 126 days, under moist and dry and sterile and non-sterile conditions (table 54).

48. In an effort to intensify the condition of contact between the active solution phase of $Ca(OH)_2$ and soil organic matter, ten soils, some acid and some alkaline, were agitated for periods of from 3 to 15 hours with *saturated* $Ca(OH)_2$, without any indication of chemical or biological decomposition of carbonaceous material (table 55).

49. Six cylinder soils treated with CaO at the rate of 4000 pounds per acre 2,000,000 pounds of soil and six soils treated with an equivalent amount of $Ca(OH)_2$ were compared with six soils which received simultaneous treatments of an equivalent amount of precipitated $CaCO_3$, after the unabsorbed portions of CaO and $Ca(OH)_2$ had become carbonated, in a comparison of the residual organic matter as influenced by the three treatments. No evidence of destruction of organic matter was adduced. A similar result was obtained in a like comparison between four treatments of CaO, four of $Ca(OH)_2$ and four of $CaCO_3$, each chemically equivalent and at the rate of 8000 pounds of CaO per 2,000,000 pounds of soil (tables 56 and 57).

50. In making the organic carbon determinations the wet combustion method of Schollenberger was modified in the absorption technic, by the use of NaOH as an absorbent. The absorption solution was washed into 500-cc. flasks, the Na_2CO_3 precipitated by the addition of $BaCl_2$, and solution made to volume; 200-cc. aliquots of the clear supernatant solution were then titrated for excess of hydrate, with phenolphthalein as an indicator.

51. The experiments as a whole point to certain definite facts which have practical application. Among these are the following:

a. CaO and $Ca(OH)_2$ in 2- to 4-ton applications will revert to the carbonate more rapidly when left on the soil surface than when mixed with a dry mulch or the moist soil.

b. If an oxide or hydrate application is left on the soil surface for several days prior to inworking, the treatment is in effect an application of finely divided $CaCO_3$.

c. Surface applications of oxide and hydrate will, for the most part, revert to the carbonate more rapidly during humid atmospheric conditions.

d. If the oxide or the hydrate is incorporated within the upper zone of the soil, prior to a more thorough dissemination throughout the soil, the concentration thus effected will bring about in the treated zone a temporary and partial sterilization which may have certain beneficial results.

e. The avidity, or affinity, of CaO is for moisture and when this is furnished by the aerial and soil atmospheres and by soil moisture, there is no tendency to effect any *chemical* disintegration of soil organic matter.

f. Neither CaO nor $Ca(OH)_2$ can be considered as chemically destructive of soil organic matter when used in the manner and in the amounts to be considered as practical applications.

ACKNOWLEDGMENT

The work reported in this publication was begun as one phase of an Adams project, at the University of Tennessee Agricultural Experiment Station, in June, 1913. It was continued and amplified while the author was in residence as a student in the Graduate School of Cornell University. The author is obligated to Dr. J. A. Bizzell for many helpful suggestions

advanced during the progress of the work. To Dr. T. L. Lyon and to the entire departmental staff, appreciation is expressed for the facilities offered and for the courteous and generous consideration accorded. Acknowledgment is also made of the material assistance rendered by Messrs. L. G. Willis and W. A. Holding, formerly of the University of Tennessee Station staff, by whom many of the analyses reported were made.

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PLATE 1

FIELD CYLINDERS USED FOR EXPOSURE OF BURNT LIME AND HYDRATED LIME (TABLES 11–21)

CARBONATION OF BURNT LIME IN SOILS

WALTER HOGE MACINTIRE

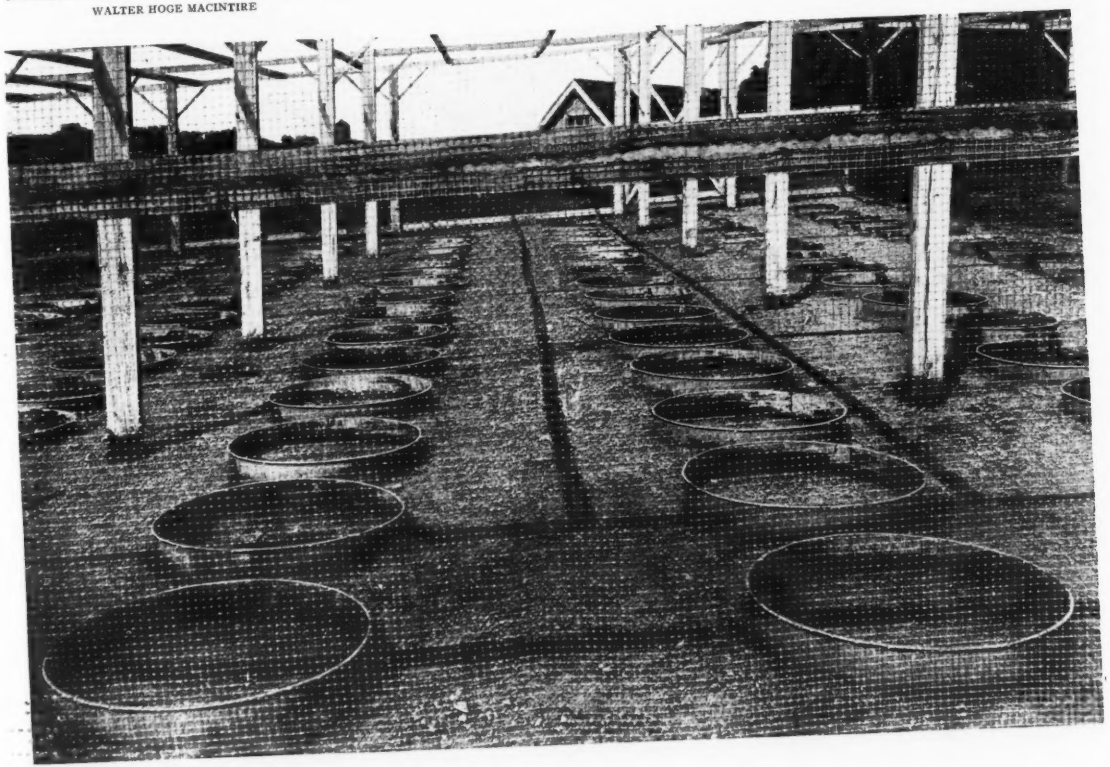


PLATE 2

FIG. 1. General view of hillside system used for exposure and leaching experiments.
FIG. 2. Inside view of hillside system used for exposure and leaching experiments.

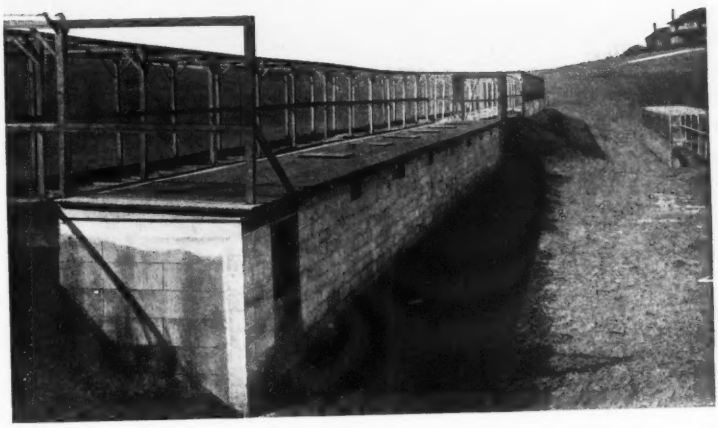


FIG. 1

FIG. 2

PLATE 3

TUMBLER EXPERIMENTS: METHOD OF EXPOSING DUNKIRK CLAY LOAM AND VOLUSIA SILT LOAM SOILS AFTER SURFACE AND MIXED APPLICATION OF $Ca(OH)_2$

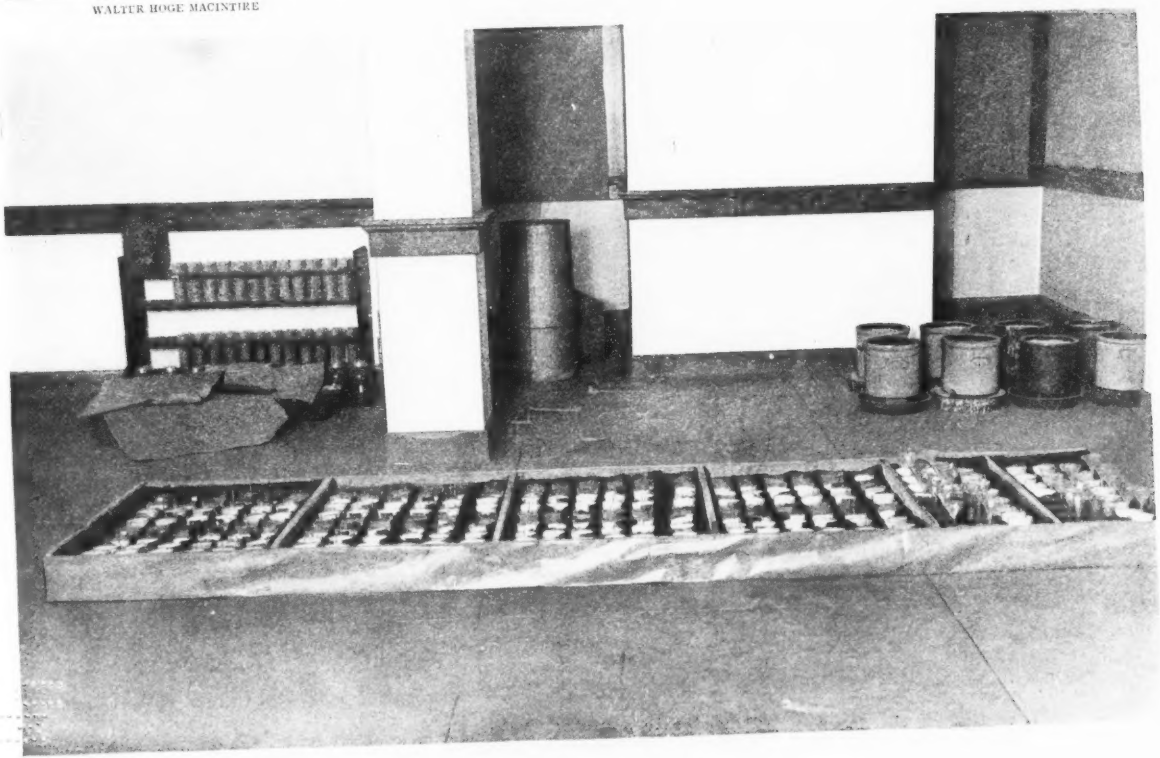
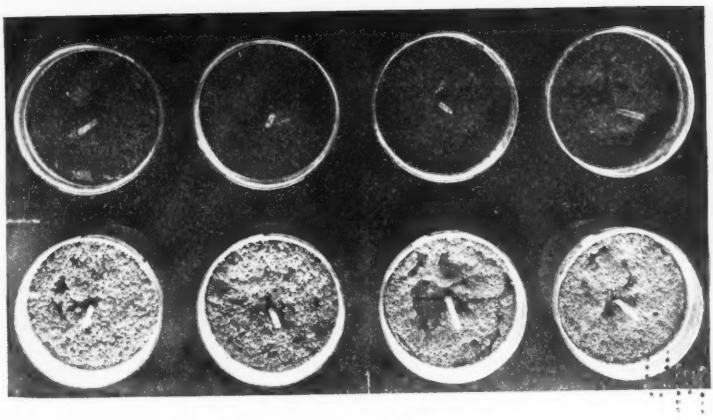


PLATE 4

SHOWING SURFACE ACCUMULATION OF PARA-FORMALDEHYDE DEPOSITED UPON THE SURFACE OF THE FORMALDEHYDE TREATED SOILS (LOWER ROW)